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PROCEEDINGS

OF THE

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OF

NEW SOUTH WALES

FOR

1940

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EDITED BY

THE HONORARY SECRETARIES.

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE
STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN.

* 1

CONTENTS.

VOLUME LXXIV.

Part I.*

Part II.†

Part III.*

* Published January 24. 1941.

Part IV.* Page.

NOTICE.

THE ROYAL SOCIETY of New South Wales originated in 1821 as the " Philosophical Society of Australasia " ; after an interval of inactivity, it was resuscitated in 1850, under the name of the " Australian Philosophical Society ", by which title it was known until 1856, when the name was changed to the " Philosophical Society of New South Wales " ; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

TO AUTHORS.

Authors should submit their papers in typescript and in a condition ready for printing. All physico-chemical symbols and mathematical formulæ should be so clearly written that the compositor should find no difficulty in reading the manuscript. Sectional headings and tabular matter should not be underlined. Pen-illustrations accompanying papers should be made with black Indian ink upon smooth white Bristol board. Lettering and numbers should be such that, when the illustration or graph is reduced to 5 inches in width, the lettering will be quite legible. On graphs and text figures any lettering may be lightly inserted in pencil. Photomicrographs should be rectangular rather than circular, to obviate too great a reduction. The size of a full page plate in the Journal is $5 \times 7\frac{3}{4}$ inches, and the general reduction of illustrations to this limit should be considered by authors. When drawings, etc., are submitted in a state unsuitable for reproduction, the cost of the preparation of such drawings for the process-block maker must be borne by the author. The cost of colouring plates or maps must also be borne by the author.

FORM OF BEQUEST.

𝕴 **bequeath** the sum of £   to the ROYAL SOCIETY OF NEW SOUTH WALES, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[*Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.*]

PUBLICATIONS.

The following publications of the Society, if in print, can be obtained at the Society's Rooms, Science House, Gloucester and Essex Streets, Sydney.

Transactions of the Philosophical Society, N.S.W., 1862-5, pp. 374, out of print.

Vols.	I–XI Transactions of the Royal Society, N.S.W., 1867–1877						,,
Vol.	XII Journal and Proceedings			,,	,,	1878, pp. 324, price 10s. 6d.
,,	XIII	,,	,,	,,	,,	,,	1879, ,, 255, ,,
,,	XIV	,,	,,	,,	,,	,,	1880, ,, 391, ,,
,,	XV	,,	,,	,,	,,	,,	1881, ,, 440, ,,
,,	XVI	,,	,,	,,	,,	,,	1882, ,, 327, ,,
,,	XVII	,,	,,	,,	,,	,,	1883, ,, 324, ,,
,,	XVIII	,,	,,	,,	,,	,,	1884, ,, 224, ,,
,,	XIX	,,	,,	,,	,,	,,	1885, ,, 240, ,,
,,	XX	,,	,,	,,	,,	,,	1886, ,, 396, ,,
,,	XXI	,,	,,	,,	,,	,,	1887, ,, 206, ,,
,,	XXII	,,	,,	,,	,,	,,	1888, ,, 390, ,,
,,	XXIII	,,	,,	,,	,,	,,	1889, ,, 534, ,,
,,	XXIV	,,	,,	,,	,,	,,	1890, ,, 290, ,,
,,	XXV	,,	,,	,,	,,	,,	1891, ,, 348, ,,
,,	XXVI	,,	,,	,,	,,	,,	1892, ,, 426, ,,
,,	XXVII	,,	,,	,,	,,	,,	1893, ,, 530, ,,
,,	XXVIII	,,	,,	,,	,,	,,	1894, ,, 368, ,,
,,	XXIX	,,	,,	,,	,,	,,	1895, ,, 600, ,,
,,	XXX	,,	,,	,,	,,	,,	1896, ,, 568, ,,
,,	XXXI	,,	,,	,,	,,	,,	1897, ,, 626, ,,
,,	XXXII	,,	,,	,,	,,	,,	1898, ,, 476, ,,
,,	XXXIII	,,	,,	,,	,,	,,	1899, ,, 400, ,,
,,	XXXIV	,,	,,	,,	,,	,,	1900, ,, 484, ,,
,,	XXXV	,,	,,	,,	,,	,,	1901, ,, 581, ,,
,,	XXXVI	,,	,,	,,	,,	,,	1902, ,, 531, ,,
,,	XXXVII	,,	,,	,,	,,	,,	1903, ,, 663, ,,
,,	XXXVIII	,,	,,	,,	,,	,,	1904, ,, 604, ,,
,,	XXXIX	,,	,,	,,	,,	,,	1905, ,, 274, ,,
,,	XL	,,	,,	,,	,,	,,	1906, ,, 368, ,,
,,	XLI	,,	,,	,,	,,	,,	1907, ,, 377, ,,
,,	XLII	,,	,,	,,	,,	,,	1908, ,, 593, ,,
,,	XLIII	,,	,,	,,	,,	,,	1909, ,, 466, ,,
,,	XLIV	,,	,,	,,	,,	,,	1910, ,, 719, ,,
,,	XLV	,,	,,	,,	,,	,,	1911, ,, 611, ,,
,,	XLVI	,,	,,	,,	,,	,,	1912, ,, 275, ,,
,,	XLVII	,,	,,	,,	,,	,,	1913, ,, 318, ,,
,,	XLVIII	,,	,,	,,	,,	,,	1914, ,, 584, .
,,	XLIX	,,	,,	,,	,,	,,	1915, ,, 587, ,,
,,	L	,,	,,	,,	,,	,,	1916, ,, 362, ,,
,,	LI	,,	,,	,,	,,	,,	1917, ,, 786, ,,
,,	LII	,,	,,	,,	,,	,,	1918, ,, 624, ,,
,,	LIII	,,	,,	,,	,,	,,	1919, ,, 414, ,,
,,	LIV	,,	,,	,,	,,	,,	1920, ,, 312, price £1 1s.
,,	LV	,,	,,	,,	,,	,,	1921, ,, 418, ,,
,,	LVI	,,	,,	,,	,,	,,	1922, ,, 372, ,,
,,	LVII	,,	,,	,,	,,	,,	1923, ,, 421, ,,
,,	LVIII	,,	,,	,,	,,	,,	1924, ,, 366, ,,
,,	LIX	,,	,,	,,	,,	,,	1925, ,, 408, ,,
,,	LX	,,	,,	,,	,,	,,	1926, ,, 470, ,,
,,	LXI	,,	,,	,,	,,	,,	1927, ,, 492, ,,
,,	LXII	,,	,,	,,	,,	,,	1928, ,, 458, ,,
,,	LXIII	,,	,,	,,	,,	,,	1929, ,, 263, ,,
,,	LXIV	,,	,,	,,	,,	,,	1930, ,, 434, ,,
,,	LXV	,,	,,	,,	,,	,,	1931, ,, 366, ,,
,,	LXVI	,,	,,	,,	,,	,,	1932, ,, 601, ,,
,,	LXVII	,,	,,	,,	,,	,,	1933, ,, 511, ,,
,,	LXVIII	,,	,,	,,	,,	,,	1934, ,, 328, ,,
,,	LXIX	,,	,,	,,	,,	,,	1935, ,, 288, ,,
,,	LXX	,,	,,	,,	,,	,,	1936, ,, 528, ,,
,,	LXXI	,,	,,	,,	,,	,,	1937, ,, 708, ,,
,,	LXXII	,,	,,	,,	,,	,,	1938, ,, 396, ,,
,,	LXXIII	,,	,,	,,	,,	,,	1939, ,, 344, ,,
,,	LXXIV	,,	,,	,,	,,	,,	1940, ,, 658, ,,

Royal Society of New South Wales

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* Resigned June 26, 1940.

† Elected July 31, 1940.

PRESIDENTIAL ADDRESS

By H. S. HALCRO WARDLAW, D.Sc. F.A.C.I.

PART I. GENERAL.

The chief events concerning the Royal Society during the year may be briefly reviewed as follows :

Owing to the uncertainty in world conditions during the early part of 1939, it was felt that the Royal Society should offer to the Government the services of its members in case of a national emergency, and a National Emergency Committee was appointed to formulate a policy for the Society. A letter was received stating that the offer of the Society's assistance was appreciated by the Government. Up to the present no call has been made upon the Society as a body. Several of its members, however, have been consulted individually, and are assisting various Government Departments in capacities for which their scientific attainments render them peculiarly suited. Most of this work is of course of a confidential nature.

The Journal and Proceedings have been published in quarterly parts, as from June 1st, in accordance with a decision made in July, 1938. This alteration has greatly expedited the publication of papers. Twenty-two papers were presented to the Society during the year.

Mr. D. P. Mellor was appointed assistant Editor of the Journal to assist Dr. C. Anderson.

The Annual Dinner for 1940 was held on March 28th, and 68 members and guests attended, the guest of honour being Sir Ernest Fisk, K.B., F.Inst.R.E., A.M.I.E. (Aust.), The Lord Mayor of Sydney, Mr. Stanley Crick, and the Minister for Education, the Hon. D. H. Drummond, M.L.A., were among the guests.

A Conversazione which it was proposed to hold in December, 1939, and to which His Excellency the Governor had accepted an invitation to be present, was, with His Excellency's concurrence, cancelled owing to the outbreak of war.

A distinguished visitor to Australia, R. Millikan, Ph.D., Sc.D., LL.D., Head of the California Institute of Technology, and an authority on cosmic rays, was entertained by the Royal Society and the Australian National Research Council in the Royal Society's rooms.

Five Popular Science Lectures were given during the winter months, and were very well attended. The lectures were as follows : " Cold Light ", by Mr. D. P. Mellor, M.Sc. ; " Whaling ", by Professor W. J. Dakin, D.Sc., F.L.S., F.Z.S. ; " The Living Soil ", by Mr. J. M. Vincent, B.Sc.Agr. ; " Nature and Nurture ", by Professor Eric Ashby, D.Sc., D.I.C., F.L.S. ; and " How Nerves Work ", by Dr. J. C. Eccles, M.B., B.Sc. (Melb.), M.A., D.Phil. (Oxon.), F.R.A.C.P. Judging by the appreciation shown by the audiences, it would seem that in sponsoring these lectures the Royal Society is helping to fill a definite need in the community and bringing to a section of the general public a better realisation of the value of science and scientific method in everyday life.

The Clarke Memorial Lecture was also very well attended, and was delivered by the distinguished visiting geologist, Sir John Flett, K.B.E., D.Sc., LL.D., F.R.S., late Director of the Geological Survey of Great Britain.

Owing to the courtesy of Mr. W. B. Clarke, a grandson of the late Rev. W. B. Clarke, photographs of the medals of the Rev. W. B. Clarke were obtained for the Society's records.

No award of the Clarke Memorial Medal was made for 1940.

The financial position of the Society, as shown by the Balance Sheet, is satisfactory. This opportunity is taken of gratefully acknowledging the indebtedness of the Society to the Government of New South Wales for the annual grant, without which the usefulness of the Society would be greatly restricted in the matter of its principal activity, the publication and dissemination of the results of scientific research conducted by its members. It was thought desirable to appoint a Finance Committee to assist and advise the Council regarding its investments, and the Executive Officers, together with Mr. E. Cheel and Mr. Allan Clunies Ross, B.Sc., F.C.A. (Aust.), were appointed a committee.

The number of exchange publications received has been 3,362. The number of societies with which we exchange

is 319, 42 of our former exchanges being in-abeyance on account of the war.

The membership of the Society as at the end of March stands at seven honorary members and two hundred and sixty ordinary members. Nine ordinary members were elected during the year, and eight were lost by resignation.

The members whose deaths are recorded with regret are :

ALFRED PAXTON BACKHOUSE, who died on August 1st, 1939, had been a member of the Royal Society since 1878—sixty-one years—and was the oldest member at the time of his death. He was born at Ipswich, Sussex, England, but came to Australia as a boy. He had a distinguished career at the University of Sydney, won several scholarships, and took his degree as Master of Arts. He was called to the Bar in 1876, and two years later was appointed Crown Prosecutor, which position he held until his appointment as a District Court Judge and Chairman of Quarter Sessions. In his capacity as Crown Prosecutor and Judge he travelled extensively in the country districts of the State, and had many exciting experiences in those early days when travel was chiefly by coach or horseback, and inundated country and rivers in flood had to be crossed by these means. He was one of the first to reach the foot of Govett's Leap on the Blue Mountains. After fifteen years of arduous country work, he was appointed a Judge in Sydney. In 1901 he was commissioned to make a special enquiry into the working of the arbitration laws throughout New Zealand.

Judge Backhouse was connected for sixty-eight years with the Anniversary Regatta, and was always a keen supporter of all forms of aquatic sports. He was also a generous patron and lover of music and drama. He was a Fellow of the Senate of the University of Sydney from the year 1887, and was also Vice-Chancellor. For the last eighteen years of his life he lived in retirement.

SAMUEL CORNWELL, who died on November 17th, 1938, but of whose death the Society was not notified until April, 1939, had been a member since 1882.

LOUIS ALBERT CURTIS died on January 13th, 1940, at the age of 84, and had been a member of the Royal Society since 1912.

WALTER WILLIAM L'ESTRANGE died on July 28th, 1939, and had been a member of the Royal Society since 1916.

He had been engaged, since his retirement, in research on the chemistry and bacteriology of brewing.

HARVEY NICKOLL, elected a member in 1924, died on September 11th, 1939.

WILLIAM J. O'LEARY died on April 16th, 1939, at the age of 70, and had been a member of the Society since 1930. He was born in Dublin, and was a son of Dr. W. H. O'Leary, M.P., himself a doctor of medicine and a well-known scientist. The Rev. Father O'Leary was educated at Tullabeg and Clongowes Colleges, and as a young man studied astronomy in Belgium, at Louvain. He carried out research work with sounding balloons in the upper atmosphere in western Ireland—work in which he was a pioneer. In 1902 he began the study of seismology, under the seismologist Mainka at Strasbourg. He set up a seismological observatory at Limerick, of which he was director from 1908, when he was appointed director of the Rathfarnham Observatory in Dublin, a post which he held until 1918. He was Professor of Mathematics and Physics at the Jesuit College at Milltown Park, Dublin.

Father O'Leary came to Australia to take charge of the Riverview Observatory in 1928, in succession to the late Father Pigot, and continued his work there until 1928 ; although he retired from the directorship, Father O'Leary continued his astronomical observations up to the time of his death. He had recently discovered new stars, with the help of a comparator designed by himself. He had invented a number of seismographs, and had worked in the last twenty years on perfecting precision time-keeping instruments. Among his inventions were a free-pendulum clock, now used for observations at Dublin, Washington and Riverview, meteorological instruments and a lighting gas plant.

Father O'Leary was a fine teacher, popular as a lecturer, and an accomplished speaker and preacher.

WILFRED JOSEPH SPRUSON, who died on August 16th, 1939, was born at Sydney in 1870, and had been a member of the Royal Society since 1917.

Mr. Spruson represented West Sydney in the State Parliament from 1897 until 1900. He was a consulting engineer, and a member of the firm of Spruson and Ferguson, patent attorneys, and had practised as a patent attorney for fifty-one years. He had received the Papal decorations of Papal Chamberlain and Cross of Leo.

SIR JOHN HUBERT PLUNKETT MURRAY, Lieutenant-
Governor of Papua, passed away suddenly in Samarai
Hospital, on February 27th, 1940, after a short illness,
while on a tour of inspection of the eastern division of the
Territory, and so died, as he would have wished, on duty.
Sir Hubert Murray was born in Sydney on December 29th,
1861, educated at the Sydney Grammar School, and then
at Oxford, distinguishing himself in the Classics.   He chose
the Law as his profession, and practised in Sydney ; he
became Crown Prosecutor and acted on occasions as a
District Court Judge.   He was Officer Commanding the
N.S.W. Irish Rifles in 1898, and saw active service in the
South African War.   Soon after his return in 1904 he
accepted the post of Chief Judicial Officer of Papua.
From that time, for thirty-six years—the first three as
Chief Judicial Officer and the last thirty-three as Lieutenant
Governor—he applied himself wholly to Papua.   Papua,
when Murray went there, was a poor and uninviting
territory, with sixty-four white residents, and would have
appeared to offer no hope of advancement to a man of his
attainments, and no scope for one of his scholarship and
culture.   In his first four years as Chief Judicial Officer,
he handled native affairs with such skill and understanding
that he was made Lieutenant-Governor.   He set to work
to build up and develop the methods initiated by the first
Administrator of Papua, Sir William McGregor.   He
gradually worked out his policy of modified direct rule,
that is direct rule based on an understanding of the natives,
his final aim being the association of Papuan and white
man in the peaceful development of the Territory.   His
methods and aims are shown forth in his annual reports
on the Territory, in his presidential address to the Australian
and New Zealand Association for the Advancement of
Science in 1932, and in his two books, *Papua or British New
Guinea* (1912) and *Papua of Today* (1925).   The results
he obtained were the peaceful pacification and civilizing
of the natives, the satisfaction of the white settlers,
co-operation with missions, and the growth of a spirit of
service among the officers of the Administration—Murray's
men.

The white population during his administration increased
to about 1,500, and he saw the natives sharing in the
development of the essential services of the Territory to
the extent of £13,000 a year through the taxes they pay,
representing part of the income gained by the 12,500 of

them who render service to white employers. He also
saw the successful working of a few village councils and the
training of two groups of Papuans in the School of Tropical
Medicine, University of Sydney, in such subjects as would
fit them for work as medical assistants among their own
people.

Sir Hubert Murray has passed on, honoured by his
King and country, and by scientific bodies, revered by his
staff, and trusted and held in affection by the natives of
Papua—the greatest honour of all to a " Ruler " of a
native people.

PART II.

SOME FEATURES OF THE EXCHANGE OF ENERGY BETWEEN MAN AND HIS ENVIRONMENT.

INTRODUCTION.

All living things are products of their environment, and
their survival depends upon their ability to maintain
certain relations with it.   The environment, however,
does not remain constant.   It is now very different from
what it must have been in the remote past, and there is no
reason for believing that slow secular changes have ceased.
It is also subject to rapid, if relatively minor variations.

The living organism is therefore faced with the problem
not only of establishing certain relations, but also of
maintaining these relations with its environment in spite
of change in the latter.   This the organism attempts to do
by variation of its own structure and behaviour.   Some
of these changes may prove favourable to its survival.
They usually result in increasing complexity of structure
and function.   One of their effects is to enable the organism
itself to exercise a certain amount of control over the
properties of its immediate surroundings.   This power has
reached its highest development in man.   He is able to
modify his environment over a range which far exceeds
that possible to other living organisms.

Even man, however, is still largely the creature of his
environment.   One of the most important of his relations
to it lies in the exchange of energy with it.   To certain
features of that exchange attention is directed in this
address.   As in Australia we have an example of the
recent exposure of a group of mankind to changed environ-
mental conditions, it will be of interest to note some of the
effects of this change.

Between man and his environment there is a ceaseless ebb and flow of energy. This interchange with his surroundings may be divided into several major phases, and in each of these phases it is subject to innumerable fluctuations. The major phases fall into three groups : one in which the exchange is increasing, one in which it remains on the whole constant, and one in which it is diminishing. The first phase may be further subdivided into a period of rapid increase, then a period of relative (but not absolute) rapid decrease in energy exchange, followed after a brief period of constancy by a slower fall in the relative energy exchange which merges into the phase of sensibly constant rate of exchange.

The three main phases of energy exchange of the body with its environment correspond to the phases of growth, maturity, and senescence in the normal course of life. The subdivisions of the period of growth are those of infancy, childhood and, following the brief disturbance of puberty, adolescence. It will facilitate the discussion of the energy relations of man to his environment if the general requirements of that useful, if evasive abstraction, an average man, are considered first. Such a man during the period of his active maturity performs a moderate amount of physical work per day, more than that performed by say a clerk or shop assistant, less than that performed by such a worker as a bricklayer's labourer or wharf lumper. A carpenter or painter would be a good representative of this typical man.

The energy requirements of this man are what he needs for the maintenance of essential bodily functions, for processes associated with the ingestion of food, for the performance of his mechanical work, and, during his immature years, for the accumulation of bodily substance in the process of growth. The energy required for mental work is not included in the categories to be considered, as it is so small that it can be neglected without error significant to purpose of this discussion (Benedict and Benedict, 1933).

An attempt has been made to represent the energy requirements of the average man diagrammatically in the text figure 1. In this diagram the scale of the abscissa is that of the chief phases of his extra-uterine life. This first phase of existence will not be considered in the present discussion. During his intra-uterine existence man does not exchange energy with the external environment, except
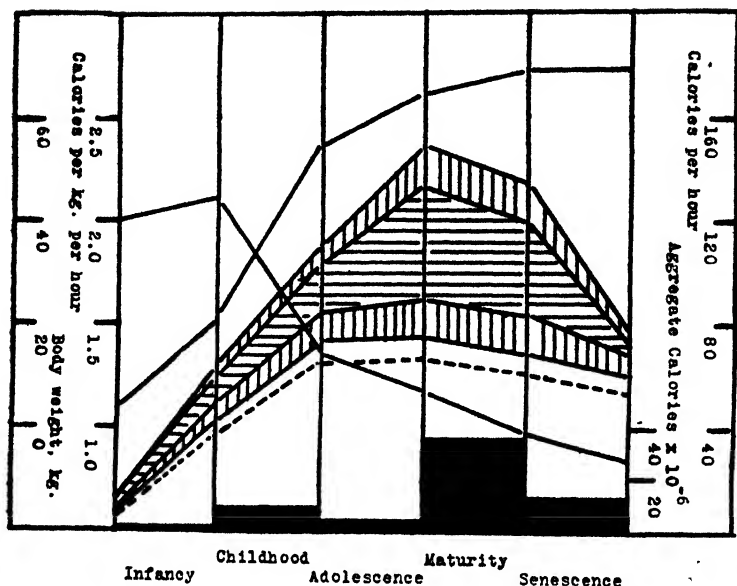
Height of black areas : Aggregate energy exchange.
Upper limit of hatched area : Total energy exchange per hour. .
Lower limit of hatched area : Resting (basal) energy exchange per
    hour, under temperate conditions.
Broken line : Rate of resting energy exchange under southern Australian
    conditions.
Height of upper vertically hatched area : Energy for mechanical
    work.
Height of lower vertically hatched area : Energy production resulting
    from ingestion of food (calorigenic action).
Height of horizontally hatched area : Heat produced as a result of
    performance of mechanical work.
Rising continuous line : Body weight in kilograms.
Falling continuous line : Energy exchange per hour per kg. of body
    weight. Quantities of energy are expressed as Calories (kilo-
    calories).

indirectly through the maternal organism. The figures
from which the various graphs have been plotted are given
in Table 1.

Two quantities not shown in the table are represented in
the diagram, namely the calorigenic action of food (or
the amount by which the energy exchange is increased by
the ingestion of food), and the exchange due to the rates of
performance of mechanical work.

One part of the energy transactions of the body has not
been represented in the above table and diagram, that is
the energy involved in the process of growth. During the

TABLE 1.

Energy Exchanges of Average Man during Extra-uterine Life.

Age.			Body Weight. (Kg.)	Calories per kg./hr. (Basal.)	Calories per kg./hr. (Total.)	Aggregate Calories.
0 Birth	..	..	3·5	2·0	7	
6 Infancy	..	.	20	2 1	42	2 5 × 10⁸
16 Childhood	..	..	55	1·35	74	8·5 ,,
20 Adolescence	.		64	1·15	74	4 7 ,,
50 Maturity	.		69	0·97	67	37·2 ,,
70 Senescence	..	.	69	0 85	59	19·4 ,,

period of growth the average man adds some 65 kg. of material to his body. About 45 kg. of this is water, which takes no appreciable part in the energy exchange when it enters the body (although it may play a very important part in this exchange on leaving the body). If the rest of the added material had undergone the normal reactions of metabolism instead of being stored up, about 120,000 Calories would have been added to the energy exchange during this period. This is less than 1 per cent. of the total energy exchange for the period of growth. It is too small a fraction of the total to represent on the diagram. This is not the total energy consumption necessary for growth but merely that diverted from other uses by the storage of material instead of its combustion. There is of course a very great variation in the rate of growth during the period from birth to the attainment of adult dimensions. During the very rapid growth of the phase of infancy the proportion of food accumulated as body substance to food metabolised with liberation of energy is much above the average. During the suckling period, for example, it is in the vicinity of 15 per cent. and may be even higher. The very slow growth of man is responsible for an energy turnover during this period some five times that of other mammals per unit of body weight.

An examination of this diagram gives the following general information about the energy relations of this average man :

The greater part of his exchange of energy with his environment takes place during the period of maturity. During this phase of his existence, his energy exchange, about 37 million Calories, is nearly twice that for the rest of his life.

This is partly due to the thirty years' duration of the period which is not far short of half his life, and partly to the fact that this is the period of maximum output of work. Next comes the period of senescence, in which the aggregate exchange from the age of fifty onwards is about half that of maturity. During this period the ability to perform physical work is waning and the energy exchange is about 17 million Calories. The time of onset of this phase is not obvious in men, and its duration varies greatly with different individuals. As shown in the diagram, however, it has not been altogether arbitrarily chosen : in considering our average man, we cannot disregard the average woman. At the age of fifty or thereabouts, following the climacteric, there is a sharp decrease in her resting energy exchange.

The energy exchange of the ten years of childhood, including the pubertal period, is about half that of our arbitrary period of senescence. The growing organism, having an average weight about half that of senescence, must have an average energy exchange about twice as rapid as that obtaining during senescence.

The small energy exchange of adolescence is partly due to the brevity of this period. The still smaller exchange of the six years of infancy is mainly the expression of the small size of the organism at this stage of growth. The actual intensity of exchange, as will be seen later, reaches its maximum in this phase.

The rate of energy exchange is seen to rise from about 14 Calories per hour at birth to a maximum of about 1,150 towards the end of adolescence. Thereafter it declines to about half this rate towards the end of the period of senescence.

The rate of resting or basal energy requirement follows a course similar to that to the total requirement. From the end of childhood onwards, however, the variations of resting or maintenance requirements are much smaller than those of the total requirements. The definite maximum at the end of adolescence does not occur and the subsequent decline is very slow. The reason for these differences is that the total energy used during the periods of infancy and of maturity is about twice that required for maintenance ; but during childhood and adolescence the total exchange is in the vicinity of one and a half times that of maintenance. During senescence the energy required for external work falls much more rapidly than

that used for maintenance, and total energy requirement approaches maintenance requirement as activity progressively diminishes.

The figures used for maintenance requirements of energy have been calculated from the figures for basal metabolism published by Boothby, Berkson and Dunn (1936) for normal males, which are expressed in terms of energy requirement per unit of body surface and time, and those collected by Boyd (1935) for the surface area at different ages. The product of the two values gives maintenance requirement of the average individual at the different ages. The figures quoted have been used as they are the most extensive series yet published. They refer, however, to individuals resident in the United States of America. The maintenance energy requirement of individuals resident in southern New South Wales is about 10 per cent. less than this (Hindmarsh, 1927; Wardlaw et al., 1934). This smaller requirement is indicated by the broken line. The total energy exchange for the performance of the same amount of external work would also be diminished by a corresponding amount under these conditions. The gross efficiency of a man performing an average amount of daily physical work should thus be about 5 per cent. greater under local conditions. The slightly lower maintenance cost in energy is due to climatic factors to which further reference will be made later.

The amounts of external mechanical work performed by this average man vary with the phase of his growth. These amounts per hour increase to a maximum which is maintained during the period of maturity and then decline during the period of senescence. The amounts are in the vicinity of 10 per cent. of the total exchange of energy.

These rates of performance of external mechanical work have been calculated by deducting from the total energy exchange (1) the maintenance rates of energy requirement, and (2) energy liberated in the assimilation of food, its calorigenic or specific dynamic action. This difference is the gross exchange of energy associated with the performance of mechanical work. The actual mechanical work is approximately 25 per cent. of this difference, assuming the now well established figures for the net mechanical efficiency of the body (Benedict and Cathcart, 1913).

The gross efficiency of a man working at the rate of our example is only about 10 per cent. For a man working

much harder, and having a total energy exchange of about 6,000 Calories per day, although the net efficiency would not be increased, the gross efficiency would be about twice as great. This is due to the fact that the maintenance exchange would be but slightly increased, and most of the extra energy exchange would be available for the performance of outside work. This would be performed at a rate four times as great as the rate of working of the average man.

The figures for the calorigenic action of food have been calculated on the assumption that an average mixed diet containing about 15 per cent. of protein was ingested by the subject, and that the calorigenic effect of protein is 30 per cent. of the energy liberated when it is metabolised. The corresponding figures used for carbohydrate and fat are less than 10 and 5 per cent. The allowance made for the calorigenic action of food is that which it would exert if no external work were performed. During work the calorigenic effect of non-protein foods can be used to supply energy for this work (Rapport, 1930). If the whole of this energy could be usefully applied, the maximum possible increase in the rate of performance of mechanical work, with the total energy exchange of the example, would be approximately 20 per cent. With higher rates of working the possible increase would be diminished.

The diagram also shows that when the energy exchange is expressed in terms of the turnover per unit of body weight per hour there is a slight increase during the period of infancy. This indicates that in spite of the rapid increase of weight during this period, and the consequent withdrawal of food to supply building material instead of energy, the total exchange of energy increases still more. During the phase of childhood, in which the increase of weight is quite as rapid, the rate of total energy exchange falls, so that at the end of adolescence it is only about half what it was at the beginning of childhood. A slow diminution of the intensity of energy exchange continues through maturity and senescence, while the body weight remains sensibly constant. (The figures used for body weight are the means calculated by Boyd, 1935, from a large series of measurements by Palmer, 1932.)

Thus, during his passage from birth to death, man's daily interchange with his environment increases at varying rates, reaches a steady value at which it remains for about half his life-time, gradually declines, and at last ceases.

From this brief survey of the general energy relations of man to his surroundings we may pass to a consideration of some special aspects of these relations. In particular it will be of interest to see what effects, if any, the conditions of life in Australia exert upon these relations.

Modes of Energy Exchange.

Intake of Energy.

Significant quantities of energy can enter the body from the environment in two ways only : directly by transfer of heat, and indirectly by the absorption of certain materials which can react with liberation of energy.

(a) *Direct.* Heat can be added to the body directly when any part of the environment to which it is exposed is at a higher temperature than the portion of the body exposed to it. One distant but very important part of the environment, the sun, is at a temperature enormously higher than that of the body. Gain of heat by radiation from this source is therefore always possible to a degree determined by the amount of radiation transmitted by the various and varying barriers of heat-absorbing material in the path of this radiation.

Heat can also be gained directly by the body when any portions of the environment in contact with it are at a higher temperature than the part of the body with which they happen to come into contact. For the greater part of his life man is not subjected to gain of energy from this source, but conditions of this kind exist in all parts of Australia from time to time during the summer months. In some parts the day temperatures may rise above body temperatures for weeks consecutively.

Energy gained from the environment in this manner is of no use to the body in its economy while the general environmental temperature is above body temperature. On the contrary, it is an embarrassment and merely adds to the total amount of energy which must be transferred to the environment to preserve the balance of income and output. An indication of this balance is the approximately constant temperature (in the vicinity of 37° C.) of the internal portions of the body.

Under conditions of low environmental temperature when loss of heat is so rapid as to become an embarrassment, the direct gain from portions of the environment which are naturally or are maintained artificially at high temperatures is of considerable use in the bodily economy. It can

compensate to greater or less extent for losses to cooler parts of the environment.

(b) *Indirect.* The whole of the energy which can be used for the activities of the body is obtained by it indirectly. It is derived from reactions between certain materials taken into the body. These materials fall into two groups : (1) a group consisting of representatives of three classes of organic compounds which form the great bulk of our food materials, and (2) the gas oxygen. It is true that many other substances must be present before reaction can take place in a suitable manner between the two groups mentioned. One of these other substances, water, must be present in quantities considerably greater than those of the reacting substances themselves. It acts, however, principally as the medium in which the reactions take place. Some of it may take part in intermediate reactions in the body, but it always is found in the end products of the reactions in the same form as that in which it occurred among the reacting substances. It therefore makes no contribution to the energy exchange.

Other essential compounds occur as minute fractions of the reacting materials. They too may take part in intermediate reactions. Their function is that of catalysts. In their absence the reactions yielding energy cannot proceed at suitable rates. Even if they took part in the final reactions their quantities are so small that they could have no significant effect on the energy exchange.

Another group of essential materials, small compared with the quantities of the main reacting materials, but much larger than the last group, consists of inorganic compounds. Some of these take part in intermediate reactions. Their principal functions, however, are to modify the properties of the medium in which the reactions occur, and to contribute to bodily structure.

Paths of Indirect Energy Exchange. The constituents of the environment which the body uses in its energy exchange are present in very varying degrees of availability. The primitive organism living in an aqueous medium environment finds its cells in contact with a medium in which all its material requirements are present in a dissolved state. The simple process of diffusion plays the most important part in the taking up of material from the environment.

The exchange of material with the environment is a much more complicated process for an organism of the size

and complexity of man.   In the first place the cells of such an organism are surrounded by an integument the chief function of which is to prevent the interchange of material with the environment.   Exchange is possible only through specialised portions of this integument.   These surfaces of absorption are part of the external surface in the sense that they are outside of the cells of the body and in contact with parts of the external environment.   They are, however, folded-in portions of this surface to which the external environment can gain access only through narrow openings, under the control of the organism.

Only one of the constituents of the environment needed by the body is in contact with the appropriate absorptive surface in a form which it can pass through this surface by diffusion and be used without some preliminary change. This is the oxygen of the atmosphere.   The other materials required from the environment are not in contact with the appropriate absorptive surfaces.   They must be brought into contact with these by the purposive activity of the organism.   For the most part they do not occur in the surroundings in forms in which they can be absorbed even when they have been conveyed to the absorptive surfaces. Usually certain preliminary changes both in their physical state and in their chemical composition are necessary.

Intake of Fuels.   The processes by which the necessary parts of the environment are brought into direct contact with the body surface in a suitable form may be lengthy and complex. They start with, perhaps, the hunting of game and the planting of crops.   They are directly responsible for a considerable proportion of the activities of the more primitive races of mankind.   Even in civilised communities much of the activity of the adult individual has the same ultimate object : the placing of certain parts of his environment in contact with certain parts of his body. But in these communities the connection is less direct. The specialised activity of certain classes enables them to collect or prepare in a concentrated state certain constituents of the environment far in excess of their own needs.   The excess accumulations of material they exchange with other members of the community, usually through one or more intermediaries, for materials which they lack. A considerable proportion of a civilised community belongs to this intermediary class.   It takes no direct part in the selection and concentration of constituents of the environment which are necessary for life.

For such individuals the intake of material from the environment consists simply of its conveyance from conveniently situated accumulations to their mouths, and from there to the absorptive surfaces. The materials are available so prepared that even the preparation of chewing before bringing into contact with the absorptive forces has become to a considerable extent unnecessary. Indeed the process of swallowing can be dispensed with should circumstances warrant it.

Even when the required constituents of the environment have been collected, concentrated, brought to a convenient state of subdivision, and placed in contact with absorptive surfaces, they are still very largely in the form of compounds insoluble in aqueous solvents. Chemical changes are as a rule necessary to convert these substances into soluble diffusible materials which can diffuse through, or at least into the integument of the absorptive surface. These changes are brought about on the surfaces themselves by the action of enzymes.

It will be noted that all these changes occur outside of the organism. They are changes imposed by the organism on the external environment, of which the contents of the alimentary tract are still a part. Only when they have passed through the epithelium of this part of the body surface are they so placed as to be able to reach the cells by diffusion. They have then passed from the external to the internal environment of the cells. The importance and distinctive character of this internal environment, as Claude Bernard (1878) long ago pointed out, is that it is a selected portion of the general environment from which non-essential and harmful constituents have been very largely excluded. The nature of this portion of the internal environment is further modified by the activity of the organism so that it becomes not only qualitatively but quantitatively suitable for the needs of the cells. Materials present in excessive concentration are either diverted to places of storage or returned to the external environment, to some extent through surfaces the function of which is essentially absorptive, but mainly through other areas of contact with the environment, surfaces of which the functions are essentially excretory.

Even when the materials selected from the environment have passed across the absorptive surfaces, there is still another barrier to be crossed before they can come into contact with the living units, the cells of the body. After

absorption these materials find themselves in the system of vessels which contain the circulating fluids of the body. They are separated from the immediate environment of the cells, the fluid which bathes them, by the walls of the vessels of the circulatory systems. Only through certain parts of these systems (the capillary blood vessels and lymphatics) is any interchange possible between the circulating body fluids and those which bathe the cells. A further degree of control is thus established over the composition and properties of the actual environment of the cells. The internal environment of Claude Bernard is thus divided into a circulating portion and a portion from which can be selected the materials in the proportions needed for the actual environment of the cells.

It will be seen that all the complicated arrangements of the control of the properties of the immediate environment of the cells of a complex organism such as man have in effect this result : the individual cells of this complex organism are rendered very largely independent of the nature of their external environment. They are preserved in surroundings which resemble closely in many ways those in which the most primitive organisms live. The complex organism as a whole is able to function successfully under a wide variety of conditions, while its individual cells continue their original primitive mode of life (Macallum, 1926 ; Wardlaw, 1929, 1930). The general principle by which increasing complexity can develop while essential primitive characters are maintained has been termed homeostasis by Cannon (1929).

Intake of Oxygen. The intake from the environment of oxygen is a much simpler process than the intake of the food materials which it reacts. This necessary constituent of the environment is always in contact with the respiratory surface through which it passes into the body. It is true that access to this surface is possible only through narrow passages. This provision is necessary for the protection of the delicate respiratory surface, and to distribute the oxygen over it. The area of this surface is some fifty times that of the outer surface of the body, but it is folded in such a compact manner as to be contained in the relatively small volume of the lungs. The unaided movement due to diffusion is not sufficient to bring oxygen to this absorptive surface at the rate at which it is required. Diffusion is supplemented by the respiratory movements which alternately bring a volume of air into contact with the

respiratory surfaces and remove it from them. The
respiratory surfaces serve for excretion as well as for
absorption. The respiratory movements assist diffusion
also in the dispersal of certain gaseous end products of
metabolism.

The intake of oxygen is further simplified by the fact
that it can diffuse through the moist respiratory surface
without undergoing any preliminary reaction. Its distribu-
tion in the circulating fluid is slightly more involved than
that of food materials. Only a small fraction of the
circulating oxygen is in simple solution. Most of it enters
into temporary combination with a protein. This compound
must dissociate before the oxygen which it contains can
again pass by diffusion to the circulating fluid, and from it
to the immediate environment of the cells. The compound
is very labile and is readily formed or dissociated in response
to comparatively small increase or decrease in the concen-
tration of dissolved oxygen in its vicinity.

Output of Energy.

Like the gain of energy from the environment, its loss
to it can occur directly, and indirectly by the loss of
material which before leaving the body undergoes a reaction
in which energy is absorbed.

(a) *Direct.* The direct loss can occur in two forms : as
mechanical work done on the environment and as heat
passing into it. The direct loss of heat, like the gain, is due
to radiation and conduction (including convection). These
forms of loss can occur only to portions of the environment
at temperatures lower than that of the body. At a
temperature of about 18° C. at the body surface, loss by
these channels from the resting body begins to take place
faster than it is produced, and activity becomes necessary
to produce heat to restore the balance. Increased loss in
this way can never become such an embarrassment to the
body as can the gain through the same channels when
external temperatures rise above that of the body. Losses
to a cold environment can be diminished by various means
such as the provision of a warmer immediate environment
by wearing clothing, and increased loss can be balanced
by the increased production in activity. By these means
external temperatures as much as 100° C. below that of
the body can be endured without harm. The upper limit
of temperature which can be successfully withstood,
however, is only about 30° C. above that of the body.

(b) *Indirect.* The indirect loss of energy occurs mainly by the loss of water from the outer and respiratory surfaces of the body. A small loss occurs in the excreta when environmental temperature is below that of the body, and by the ingestion of food and drink cooler than the body. At low external temperatures losses by these means might become important, but under ordinary conditions of comfort they can hardly amount to 10 per cent. of the total energy exchange.

The chief indirect loss of energy is due to the loss of water which changes its state as it leaves the body. This mode of loss may be regarded as the reverse in kind by which the body gains energy by ingesting materials which combine within it with liberation of energy. Liquid water at body temperature exists mainly as a mixture of dihydrol $(H_2O)_2$ and trihydrol $(H_2O)_3$. On evaporation these molecules dissociate into molecules of monohydrate with absorption of energy derived from the body. The quantitative importance of these energy changes accompanying the reaction in maintaining the energy balance of the body under certain environmental conditions will be considered later.

Variations of Rate of Intake and Output of Energy.

The rate at which the body gains energy from the environment varies greatly from time to time during the course of the day. The temperature of the environment, for example, changes considerably between day and night, with corresponding variations in the rate of direct interchange of energy. The fluctuations can be minimised in proportion to man's control over his environment. This control is very complete in the case of civilised man. With him the fluctuations of direct energy exchange are, or can be made, a small fraction of his total exchange.

This is not true of the indirect gain of energy. Although the fluctuations of this part of his energy exchange are under man's control, the fluctuations must necessarily be very great. Periods during which there is rapid intake of materials which can react with liberation of energy alternate with periods in which there is no intake of one or more of the reactants.

These reactants are oxygen and various oxidisable constituents of the food materials. The reactions which occur lead eventually to the oxidation of these materials : to the complete oxidation of the non-nitrogenous organic

materials, to the incomplete oxidation of nitrogenous organic materials. It may be recalled, however, that these reactions take place in several stages. Varying amounts of energy are involved at each stage in the different reactions. Some of these reactions do not involve oxidation even in the wider sense of dehydrogenation, which is such a frequent type of intermediate reaction. The principal reaction by which energy is obtained for the performance of mechanical work on the environment, in fact, does not involve oxidation. It is a hydrolysis of an unstable compound, that is to say of a compound which tends to decompose with liberation of energy. The real intake of energy which can be converted into mechanical work is, therefore, the intake of the compounds which react to build up this unstable compound. Their reactions are essentially oxidations. It is apparent therefore that the rate of indirect intake of energy from the environment is rather difficult to define from moment to moment. The rates of intake of the various reactants and the rates at which the different stages of their interaction occur may differ widely.

The difference of behaviour of these two classes of material, oxygen and oxidisable substances, though striking, is only quantitative, and is dependent on the different storage capacity of the body for them. Under normal conditions very considerable stores of combustible material are present in the animal body. In man they are sufficient to sustain life, at a low level of physical activity, for over a month (Benedict, 1915 ; Labbé and Stevenin, 1922). The dog can survive on these stores for over three months (Howe, Matill and Hawk, 1912), with no apparent ill effects. Poikilothermal animals, with their low average level of energy consumption, normally ingest food only at intervals of weeks, or even months.

The stores of oxygen which can be accumulated are on the other hand very small. Under extreme conditions man's requirements during rest can be met from these stores only for a period of about four minutes. Certain diving mammals such as the whale can carry on moderate activity for about thirty minutes on their stored oxygen (Irving, 1939).

Although the stores of oxygen in the body are small, they are essential. One distinction between a higher living organism and a primitive organism, or an inanimate energy transformer, is the internal environment which is

so characteristic of the higher organism. It is from the materials in or readily accessible to this internal environment that the cells of the higher organism draw their supplies. Upon these stores accumulated within its body the higher organism is entirely dependent for its immediate needs. Some of the stores of food material within the body are obvious enough. The store of oxygen in the oxyhæmoglobin of the blood, although much smaller, and that dissolved in the blood, which is of a still lower order of magnitude, are also well known. The importance of yet another store of oxygen of a lower order of magnitude again has recently been shown by Millikan (1939). This store is present in the muscle cells themselves, in a form of combination similar to that in oxyhæmoglobin. The store present varies with the habitual activity of the cell. For example, in heart muscle, in which the twitch is relatively very slow and may occupy about half a second, the amount appears to be in the vicinity of that required by the performance of a single contraction, the unit quantity of work which it is able to perform. Those stores of material which will supply the needs of the body for periods measured in fractions of a second are, if anything, more important than those which will meet its requirements for weeks. Intracellular stores are the only stores of material available to the primitive organism. They play a very intimate part in the activity of the cell. They therefore constitute a more fundamental requirement than those stores which the more complex organism accumulates in its internal environment in the process of rendering itself more independent of the nature of its external environment.

The ultimate limitation to the activity of an organism whether simple or complex is the rate at which these intracellular stores of material can be renewed. And it must not be forgotten that the problem of maintaining the supply of necessary material is bound up with another problem, that of the disposal of the end products of the reactions by which these materials yield energy. The rate at which these reactions can occur is a function of the ratio of the concentration of the reacting substances to that of the products of the reaction. No doubt analogies can be found in inanimate energy transformers, but this close relation between material and the mechanism using it, between the machine and its fuel, is a very striking feature of the living organism.

Although there is this close relation between intake and output of energy in the individual cell, these two processes have a considerable degree of independence in the complex organism considered as a whole. This independence is in part due to the possibilities of storage of materials in the internal environment as has been indicated, and partly to the fact that there is no storage of the energy produced during the activity of the body, nor of the end products of the reactions from which this energy is derived. The output of energy into the external environment, whether direct or indirect, therefore stands in closer relation to the activities of the cells than does the intake of energy.

The range of variation of energy output is further limited by the fact that even the resting cell has a certain exchange of energy. Even when the organism as a whole is at rest in the sense that it is performing no mechanical work upon its external environment, a certain proportion of its cells are always in a state of activity, performing work upon the internal environment. Our "average man", it was seen, when working only produced energy about twice as fast as when resting. In short bursts of extreme activity lasting only a few seconds the rate of output of energy can be forced up to about one hundred times the resting rate (Furusawa, Hill et al., 1925).

Such a rate of output of energy far transcends the greatest possible rate of intake of oxygen and of oxidisable material. Oxygen can be absorbed for short periods at ten times the basal rate or slightly faster (Henderson and Haggard, 1924). Less is known about the maximal rate at which oxidisable material can be absorbed after the material has been brought into contact with the appropriate portion of the alimentary surface. Trimble, Carey and Maddock (1933) have shown that the simplest and probably the most rapidly absorbed of these materials, glucose, can be absorbed by the dog at the rate of about 1 gramme per hour per kilogram of body weight. If this figure can be applied to man, which is doubtful, the intake would be at a rate sufficient to permit an energy production at about four times the basal rate. The body is therfeore forced to draw upon its extensive stores of fuel much sooner than upon its meagre store of oxygen.

At an extreme rate of activity the human body may thus transform energy about five times as rapidly as it can obtain the oxygen needed to sustain such a rate of activity and about twenty-five times as rapidly as it can obtain the

necessary fuel in the form of carbohydrate from the environment. If the fuel were in the form of fat a given intake would correspond to more than twice the energy exchange associated with the combustion of carbohydrate, but it is not likely that fat would be absorbed as rapidly as a simple monosaccharide. Even at a rate of working with which the oxygen supply can keep pace, the consumption of fuel must be twice as rapid as the maximum rate at which it can be obtained from the environment.

Having thus briefly considered certain of the fundamental conditions which limit the rate of energy exchange of an individual in either direction, we may turn to consider how the exchanges of different individuals differ, and what are the principal causes of such differences as may appear. It is necessary first to lay down some basis upon which the energy exchange of the different individuals may be compared.

Comparison of Energy Exchange of Different Individuals.

From the foregoing discussion it is evident that the principal causes of variation of the energy exchange of an individual are variations in the rate of performance of external work and in the rate of intake of food. These two factors must be known and comparable before comparisons between the energy exchange of individuals are possible. The simplest condition in which these two factors become comparable is that in which their effects have been eliminated. Comparisons are therefore usually made when individuals are in a state of complete rest and when the more immediate effects of exercise and of the ingestion of food have passed off. Variations of external conditions such as temperature, air movement, disturbance, which are likely to affect the energy exchange, must also be excluded. Under these conditions the subject is said to be in the basal state, a condition of energy exchange with the environment which is reproducible with considerable accuracy, and therefore a suitable basis for comparison.

Even when these conditions are fulfilled, variations due to the age, sex, and size of the individual must be taken into account. Only persons of the same sex and age are strictly comparable. The general effect of age has already been indicated. For the present purpose the effect of sex may be summarised by the statement that the resting

energy exchange of the human female is on the average some 10 per cent. lower than that of the comparable male.

The choice of basis on which the energy exchange of comparable individuals of different size may be compared is not so simple. Where the difference of size is great, as between animals of different species or off different ages, the unsuitability of the energy exchange per unit of weight as a basis of comparison is immediately obvious. The exchange in the smaller animals is much more rapid than in the larger. This fact was established in the very early days of quantitative experimentation on the energy exchange of animals (Regnault and Reiset, 1849).

A monumental output of work on this subject has come from the Nutrition Laboratory of the Carnegie Institution of Washington for the last quarter of a century. This work has recently been reviewed by Benedict (1938) who himself did most of it and inspired the rest. Warm-blooded animals ranging from mice weighing 8 gm. to horses weighing 700 kg. were examined. Even an elephant weighing 4,000 kg. was examined, but the measurements made upon it are not regarded by Benedict as numerous enough for inclusion in the general comparison.

There is some doubt as to whether all these animals were strictly comparable with regard to their state of activity and nutrition, and the temperatures of their environments. In spite of these limitations, and some uncertainty as to the accuracy of measurement of their surface areas, Table 4 of Benedict's review shows that the average energy exchange per unit of body surface has a coefficient of variation of only 38·2 per cent. The energy exchange per kilogram of body weight on the other hand ranged from 17 to 125 Calories per 24 hours. Comment upon this seems to be unnecessary.

When, however, the comparison is made on the basis of surface area, the uniformity becomes as striking as was the variation when the unit of body weight was used for comparison. The range between, say, the horse and the hen becomes only a few parts per centum instead of some seven times, as it was on the basis of weight (Voit, 1901). Such comparisons must of course be limited to homeo-thermal animals. The body surface used for this comparison is the external surface of the body normally in free contact with the external environment. It does not include the alimentary and respiratory surfaces, which are

of much greater area but are in contact with the environment only in a restricted sense.

Where the range of variations of size is small, as among the adults of one species, the difference between comparisons of energy exchange based on body weight and those based on body surface must obviously be smaller. Indeed, when measured over a small enough range all variables vary approximately proportionally to one another. It would be a matter of indifference which bodily measurement was used as the basis of comparison of the energy of individuals within this range of size. Much of the controversy which has continued for so long on the relative merits of body surface and of body weight for comparisons of energy exchange seems, therefore, to be without point. This aspect of the question has been well discussed by Murlin (1921) and by Du Bois (1937).

The possibility that some empirical function of size, more or less closely related to the body surface, such as the 0.7 power of body weight, may give a slightly better correlation between size and energy exchange, is also without significance for the purpose of this discussion. The recent work on this point has been well reviewed by Brody (1934).

More cogent objections to the use of the unit of surface area as the basis for comparison of energy exchange are the practical one that the surface area is very difficult to measure, and the theoretical one that there is no physical basis for the choice of this unit. There is a natural tendency to associate the area of surface in free contact with the external environment with the rate of exchange of energy, especially heat, with the environment. Rubner (1883), to whom we owe mainly the development of the use of the unit of external body surface for comparisons of energy exchange, certainly was at first under the impression that body surface was an important factor in the loss of heat by radiation. But, as has been pointed out, a restricted exchange also takes place across the respiratory and alimentary surfaces, but no suggestion has been made that these surfaces also should be considered in comparing exchanges of energy. Loss by radiation from a homeothermal animal depends on the temperature of the environment, and it was later shown in his laboratory that rate of heat loss within certain limits was independent of the external temperature. The development of our knowledge of the relation of external surface area to energy

exchange was reviewed by Rubner (1931) shortly before his death.

Further the radiating surface of the body is not the same as its total external surface : it depends upon posture. Attempts have been made to measure this radiating surface by determining the electric charge which the body can acquire under standard conditions (Bohnenkamp and Pasquay, 1931), and by observing the loss by radiation under conditions in which the loss from unit area was known (Winslow, Gagge and Herrington, 1939). Both methods gave a result of about 75 per cent. of the total surface for the radiating surface of the human body in the erect posture.

Apart from the convenience and simplicity of the measurement of weight and the fact that it may afford as good a basis as body surface for comparison of energy exchange within a species (Harris and Benedict, 1919 ; Bjerring, 1931 ; Adams and Poulton, 1935), the principal argument of its supporters is that energy exchange must be a function of the amount of actively metabolising tissue in the body, and that this must be more closely related to weight than to surface area. Even if the last assumption be accepted, it must be admitted that the proportion of active to relatively inactive tissue (*e.g.* fat) may vary considerably among individuals of the same weight. At present the measurement of the proportion of fat in the living body is much more difficult than the direct measurement of surface area. The proportion of fat in the body can be assessed approximately by measurement of the specific gravity. Bohnenkamp and Schmäh (1931) have shown, however, that this measurement, although very simple in principle, is attended with very great difficulty when applied to the living body.

The practical difficulties of the measurement of surface area were removed when it was shown by Du Bois and Du Bois (1916) that the body surface of man can be calculated simply from measurements of height and weight by means of their now almost universally employed formula : surface area (cm.^{2})=height$^{0.725}$ (cm.) $\times$ weight$^{0.425}$ (kg.) $\times 71 \cdot 8$. The demonstration of this extremely useful relation was the happy result of cooperation between a physician and an engineer.

There seems then to be no good reason for departing from this simple commonly used unit of comparison, surface area, which has such obvious advantages for

comparisons of energy exchange of different individuals, or animals varying widely in size, because the advantages are not as obvious when the variations of size are smaller.

When a satisfactory basis for comparison of the energy exchange of individuals has been attained, another difficulty presents itself. Measurements of energy exchange on normal individuals, like all other measurements made upon them, show a certain range of variation. Even the same individual, when measured on different occasions under conditions made as strictly similar as possible, shows a range of variation in the values obtained. Under such conditions all the values occurring within the range observed are regarded as normal simply because no reason for the variation is apparent. Until recently our knowledge of the extent of these " normal " variations was rather vague owing to the paucity of strictly comparable data. It has now been put upon a more satisfactory basis by statistical examination of the extensive material accumulated at the Mayo Clinic by Boothby and his associates (Boothby, Berkson and Dunn, 1936 ; Berkson and Boothby, 1937). Cognisance of these normal ranges of variation must be taken in considering the effect of any environmental factors upon energy exchange.

The factors which affect the level of the energy exchange between an individual under standard conditions and his external environment fall into two groups : those resulting from relations with the environment which are directly under the control of the individual, and those which are not directly under his control.

By far the most important of the first group of factors are the effects of the level of intake of energy, or of materials which can react with liberation of energy, and the performance of mechanical work upon the environment. The direct effects of these activities are of course not meant. These have been mentioned and are directly proportional to the extent of the activities in question. What is meant is the more remote effects of these activities. It has already been indicated that ingestion of food increases the energy exchange of the body quite apart from the utilisation of the food as a fuel. Similarly the performance of mechanical work shows an effect on the level of the energy exchange long after the immediate effects of the work have ceased. In short, even under strictly comparable conditions of rest the level of the energy exchange of a well nourished

active individual is higher than that of a less active individual living at a lower plane of nutrition.

Another factor must also be considered when the energy exchange of otherwise comparable individuals is examined. This is the effect of race. The effect of this factor is very difficult to disentangle from others depending on the relation of the individual to his environment. Further reference will be made to this later.

The principal environmental effect which varies independently of the actions of the individual is that of climate. In this must be included all those factors due to geographical position, seasonal effects, and weather.

EFFECT OF AUSTRALIAN CLIMATIC CONDITIONS ON HUMAN ENERGY EXCHANGE.

In considering the effect of the climate of Australia on the energy exchange of its human inhabitants, the large area of the continent must be borne in mind. It extends, roughly, between latitudes 10° N. and 44° S., and between longitudes 153° E. and 112° W. More than a third of the total area lies within the tropical zone, the rest in the temperate zone. In each zone there is a range of climate varying from humid to arid, from coastal to upland.

Associated with this wide range of climate is a wide range of seasonal variation. The mean monthly temperature at Darwin, for example (12° 28′ S., 130° 51′ E.), has a range of less than 5° C. The range at Alice Springs (23° 28′ S., 133° 37′ E.) is four times as great. The mean monthly relative humidities of these two situations range from a maximum of 90 per cent. in the first to a minimum of 10 per cent. in the second. In some inland regions the maximum daily temperature may exceed 38° C. (100° F.) for weeks consecutively (e.g. Marble Bar), and may reach 65° C. ; in other parts (south-eastern New South Wales) it may fall at times below —17° C. (0° F.).

Although the veteran Dutch investigator Eykman (1896, 1921) long denied stoutly that climate as such has any effect on human energy metabolism, and Benedict and Gustafson (1928) made observations which throw doubt on the effect of seasonal variations of climate, most other investigators have obtained results which show an effect in the direction which might be expected on theoretical grounds. Lower temperatures are usually associated with increased rate of energy exchange. The figures which are used for comparison of energy exchange are based on

observations made on individuals living in the north-eastern portion of the United States of America. The extreme range of variation from these figures which have been observed are from 30 per cent. above them for Eskimos in Baffin Land (Heinbecker, 1928, 1931 ; Rabino-witch and Smith, 1936) to 30 per cent. below them for Australian aborigines in the north coastal region of New South Wales (Wardlaw and Horsley, 1928). Such extreme figures, however, cannot be attributed entirely to the effect of climatic differences. They include effects which may be due to differences of race, diet and habits of life.

Martin (1930) has shown a very definite and rapid effect of variation of climate in a series of determinations of his own resting energy exchange during a voyage from England to Australia. On entering the tropical zone his energy exchange began to fall from its usual level of 60 calories per hour until a figure 10 per cent. lower was reached. At this level it remained during his stay in Australia, but rose to its first level during the return journey.

With respect to the effect of seasonal variations of climate Gessler (1925) has shown a rise of some 10 per cent. in the rate of resting energy exchange between the German summer and winter.

A climatic effect is also to be seen in the measurements of basal energy exchange of white Australians. Hindmarsh (1927) and Wardlaw, Davies and Joseph (1934) found values in Sydney 10 per cent. lower than the standard figures for temperate climates. Sundstrom (1926) found values in tropical Australia (Townsville) which are about 20 per cent. below the standard figures. The observations which have been made in Australia on the energy exchange of man therefore support the general conclusion that energy exchange in the resting state falls as the temperature of the environment rises, so long as this rise is not great enough to prevent the maintenance of an energy-balance with the environment.

Further evidence of a climatic, or at least a seasonal, effect on the rate of energy exchange, is shown by observations made on two comparable groups of full-blood aborigines. One group of twelve males examined during the early spring when the mean daily temperature was 13·5° C. gave an average basal rate of exchange 9 per cent. below the standard figures for whites in a temperate climate (Wardlaw and Lawrence, 1932). The other group of ten males examined about the middle of summer at a

mean daily temperature of 25·6° C. showed an average basal energy exchange 18 per cent. below the standard figure (Wardlaw, Davies and Joseph, 1934). A third group, which gave the very low figures already cited (Wardlaw and Horsley, *loc. cit.*) is not comparable with these two owing to wide difference between their states of nutrition and activity.

THE DISTRIBUTION OF ENERGY EXCHANGE.

Certain climatic factors of the environment, notably the temperature, and to a much less important extent the humidity and movement of the atmosphere, affect not only the rate of energy exchange with the body, but also the distribution of this exchange between various paths. At temperatures below that of the body environmental conditions have no direct effect on the gain of energy by the body. At higher temperatures the whole of the loss, apart from mechanical work on the environment, occurs by evaporation of water from the external and respiratory surfaces of the body. At lower temperatures the loss by this means varies.

Exchange of Energy by Evaporation.

It is now well established that in a temperate climate (north-eastern United States), when the measurements are made at a laboratory temperature between 18° and 26° C., about one-fourth of the total loss of energy of normal man takes place by evaporation. This has been shown both by the classical direct measurements of the water given off (Benedict and Carpenter, 1910 ; Soderstrom and Du Bois, 1917), and indirectly by measurement of the so-called insensible loss of weight of the body, due allowance being made for the small changes of weight due to difference between weight of oxygen taken in and carbon dioxide given off (Benedict and Root, 1926). Under these conditions of environmental temperatures the loss by evaporation from the skin is rather greater than from the respiratory surfaces of the body (Benedict and Benedict, 1927). This means that the average loss from unit area of the skin is at least fifty times as rapid as from an equal area of respiratory surface. The loss from the skin is not uniformly distributed over its surface but is about three times as rapid from the palms of the hand and soles of the feet as from the rest of the body surface (Benedict and Wardlaw, 1931). At temperatures below the range stated

the absolute amount of energy lost by evaporation falls only slightly. At these lower temperatures, however, the total loss of energy may rise considerably owing to increased loss of heat by radiation, conduction and convection, and the proportion of heat lost by evaporation may therefore undergo considerable diminution. The loss of energy by evaporation within and below the range of temperature mentioned is a purely physical process, which is not even affected immediately by the death of the subject.

Rise of temperature above this range produces an immediate and striking effect. Within a rise of one degree at the upper limit of this range of external temperature there is a sharp increase in the loss by evaporation. This rises with external temperature until at a value a few degrees below that of the body temperature evaporation accounts for the whole of the heat lost from it. Exercise tends to increase the proportion of heat lost by evaporation. An examination of published data by Heller and Schwarz (1930) showed that the increase appeared at a rate of working about twice the basal rate of energy exchange.

It is at first sight surprising to find that loss of energy by evaporation is so little affected by the humidity of the atmosphere. Below the external temperature of 25° C. variations of relative humidity of the atmosphere as wide as from 12 to 88 per cent. are practically without effect on the loss by evaporation (Winslow, Herrington and Gagge, 1938). Above this temperature evaporative loss increases more rapidly at high than at low relative humidities and becomes inadequate to maintain the energy balance between subject and environment at a temperature near that of the body. At low relative humidity and with the protection against gain of energy by radiation and conduction afforded by clothing, evaporation can maintain a balance of energy exchange up to an external temperature of 52° C. This independence of the humidity of the atmosphere on the part of loss of energy by evaporation was shown to be due to the effect of air movement (Winslow, Gagge and Herrington, 1939). Velocities of air movement so slow as to be subjectively imperceptible increase the evaporative power of the atmosphere to such an extent that variations of humidity become of little significance. Even in still atmospheres an effective degree of air movement near the skin occurs as a result of convection currents

except when the temperature of the air is very close to that of the skin.

Very few observations have so far been published of energy loss by evaporation in Australia. The results obtained indicate the loss under basal conditions tend to be in the vicinity of 30 per cent. of the total loss for white Australians. The proportion of the evaporation from the skin to the total is also higher than that found in temperate regions, being over 70 per cent. The temperatures at which the observations were made sometimes approached that at which the sudden increase of evaporative loss begins. This fact, and the fact that the temperatures to which the subjects were exposed during later periods of the day often exceeded this temperature, may account for the variability of these results and their tendency to higher values.

Observations on Australian aborigines indicate that in them, under basal conditions, evaporation may play a still more important part in the energy exchange (Wardlaw, Davies and Joseph, 1934). The average temperature at which the observations on these subjects were made was 26·8° C., that is slightly above that at which increase of evaporative loss begins. When all observations made at temperatures above 26° C. are excluded, however, the proportion of energy lost by evaporation still has an average value over 35 per cent. of the total. The proportion of loss from the skin to that from the lungs is similar to that for the whites.

While there may be some doubt as to the effect of climatic conditions on basal losses of energy by evaporation under Australian conditions, or even as to the difference between whites and aborigines, the differences become more striking when total daily losses are compared. For example, a group of four whites was observed carrying on the same activities for periods during which the mean maximum daily temperatures were 19° C. and 28° C. respectively. The average daily losses by evaporation were 386 and 930 Calories per sq. m. respectively. A group of aborigines examined with the whites under the hotter conditions lost an average of 1,165 Calories per day per sq. m. of body surface, although the activity of the aborigines was less than that of the whites.

Under the hotter conditions the whites lost more than twice as much energy by evaporation as under the cooler. Under comparable conditions the aborigines lost at least

25 per cent. more energy by evaporation than the whites. When a white and an aboriginal performed mechanical work at similar rates (walking at the same speed) while exposed to the sun, the rate of loss of energy by evaporation was 34 per cent. higher in the black than in the white.

It is interesting to note that Martin (1931) found that the rate of absorption of solar energy by the skin of a negro was 30 per cent. greater than by the skin of a white man. The greater rate of loss by evaporation from the black skin would seem to balance the greater rate of absorption of radiant energy from the sun. Such a provision does not appear to give the black any advantage in the maintenance of his energy balance. The physiological advantage of the pigmented skin may perhaps be associated with a protection of deeper tissues by the absorption of a greater proportion of the sun's rays in the more superficial layers of the body. Hardy (1934), however, found that artificially blackened absorbed infra-red radiation no faster than white skin.

Evaporation and Direct Gain of Energy from the Environment.

The range and flexibility of evaporation as a means of adjusting the balance of energy exchange is well shown by the following experiment (Wardlaw, Davies and Joseph, 1934). The experiment also shows the difference of response of the white and the aboriginal to the range of environmental conditions to which each was exposed. The energy output and loss by evaporation of the nude subjects were measured first under conditions as near to basal as the circumstances permitted. The loss by evaporation was then measured at a shade temperature of $45° \cdot 2$ C., and finally when the subjects were exposed to the sun. The accompanying figures give the energy losses in Calories per sq. m. of body surface per hour.

Effect of Temperature and Solar Radiation on Loss of Energy by Evaporation.

Energy Lost (Calories/m.²).

	Total. (Temperature $24 \cdot 8$–$27 \cdot 3°$ C.	Evaporated.	Evaporated. $45 \cdot 2°$ C.	Evaporated. In Sun.)
White	$37 \cdot 3$	$8 \cdot 7$	$32 \cdot 2$	339
Aboriginal	$32 \cdot 5$	$12 \cdot 3$	$31 \cdot 4$	371

The energy lost by evaporation rose with temperature from $0 \cdot 23$ and $0 \cdot 37$ of the initial resting values to $0 \cdot 86$ and

0·96 of these values. On exposure to the sun for half an hour the rates of evaporation rose to 9·1 and 11·4 times the initial total rate of energy loss. The last figures were 39 and 30 times the initial rates of evaporation. The figures indicate that while exposed to the sun these subjects were absorbing energy at a rate similar to the rate of production of energy of a man performing strenuous physical work.

Under conditions not uncommon in many parts of Australia direct absorption of energy from the environment may therefore be the dominating factor in the energy exchange of man. In the experiment described the mechanism for the maintenance of a balance between intake and output of energy was strained beyond its capacity. The temperatures of the subjects during their exposure to the sun were rising at an average rate of approximately 0°·3 C. per hour. From this figure it may be calculated that the subjects were gaining energy at a rate of over 20 Calories per sq. m. per hour faster than they were losing it.

Such conditions could not be long endured without a dangerous rise of body temperature. The performance of mechanical work with its accompanying production of heat equivalent to three times the amount of the·work, throws a severe additional burden on the mechanism for the regulation of energy exchange. Vigorous physical work is possible under these conditions only for brief periods, and these periods must be interspersed with periods of rest in the shade long enough to allow the temperature of the body to return to its normal value. Water must be ingested at frequent intervals to replace that lost. The difficulty of maintaining the balance of energy exchange when heavy work is performed even under much less severe conditions than those of the above experiment may account for the discontent with their lot which is so prevalent, for example, among wharf labourers in tropical ports of Australia.

Under the conditions of the experiment cited the total losses of water per hour during exposure to the sun were at the rates of 1,140 and 597 gm. per hour (surface areas of subjects, 2·09 and 1·61 sq. m.). To maintain the balance of energy exchange during vigorous work, it would be necessary for these rates of loss to be doubled. The figures quoted emphasise sufficiently the very great importance of an adequate supply of water to the organism exposed

to these conditions of high temperature and absorption of solar radiation. In addition water is required for the solution of the materials which are excreted from the body in the urine, and a smaller quantity is lost with the fæces. Davies (1935) found that the losses by these channels under rather less severe conditions of temperature, but with the performance of a moderate physical activity, were in the vicinity of 600 ml. per day. Some years ago Hunt (1912) found an average hourly loss of 570 ml. from Europeans under similar conditions in the Deccan.

Davies (*loc. cit.*) also made the interesting observations that aborigines living under such conditions were able to excrete a distinctly more concentrated urine than visiting whites. The economy of water which could be effected by this means is certainly small, but the existence of this difference points to an adaptation to the conditions of the environment. Unfortunately these conditions which call for abundant supplies of water to replace the loss from the body are often encountered in environments in which the scarcity of water is an outstanding feature.

The importance of stores of various materials in the body for meeting the demands of rapid production of energy has been indicated. The store of water in the body is no less important under conditions of rapid production or absorption of energy. Although about two-thirds of the body consist of water, only a small fraction of this water is available for adjustment of the energy balance. The considerable stores of fat and carbohydrate in the well-nourished body may be reduced to small fractions of original amounts during periods of under nutrition. Loss of even 10 per cent. of the body water on the other hand shows its effect on the functioning of the living body. Deprivation of water can be survived for only some three days as against the period of over a month's deprivation of food which man can survive without permanent ill effects.

One of the factors determining the rate at which water evaporates from the body is the difference of vapour pressure between the surface of the body and the atmosphere in contact with it. This difference is a function of the humidity of the atmosphere and the vapour pressure of the evaporating body fluid. Rise of the vapour pressure of this fluid increases the rate of evaporation under comparable conditions. Such an effect would be brought about by a dilution of the body fluid. A dilution and rise of the

vapour pressure of the blood of a warm blooded animal
(cat) was shown by Barbour and Gilman (1934) to be one
of the first effects of exposure to rise of temperature of the
environment under rather severe experimental conditions.
After a period of exposure to such conditions, however,
the reverse state of affairs supervenes : the body fluids
become more concentrated and their rate of evaporation
falls.

The first of these changes would appear to be the
response of the mechanism for the maintenance of balance
of energy exchange ; loss of energy by evaporation is
facilitated by the raised vapour of the evaporating fluids.
The second phase of the response is probably indication
of the limitation of the available store of water, and of
the fact that maintenance of the osmotic properties of the
circulating fluids of the body is of more fundamental
importance than the maintenance of its energy balance.

Similar effects are clearly seen in man (Wardlaw, Barry
et al., 1935). A group of five laboratory workers, for
example, were transferred from an environment having a
mean diurnal temperature of 19° C. (Sydney) to one having
the corresponding temperature of 28° C. (Hermannsburg,
Central Australia). Under similar conditions of activity
the concentration of the blood of every member of the
group fell in the hotter environment. The average fall
for the group was from 23·5 to 21·7 gm. of solids per
100 ml. of blood. When, however, more strenuous work
was carried out, partly while exposed to the sun, the blood
became more concentrated, the average rise for the group
being from 21·7 to 24·3 gm. per 100 ml. A group of
aborigines who were exposed to the latter conditions
showed only an insignificant rise of concentration of their
blood (22·2 to 22·6 gm./100 ml.). The figures indicate also
the better adaptation of the aborigines to these conditions.

Young, Breinl et al (1920) also found a concentration of
the blood of whites under similar conditions in north
Queensland. Although these figures do not reveal the
change of actual concentration of solutes in the blood, the
variation is highly suggestive of the response observed
under experimental conditions in animals.

Distribution of Indirect Gain of Energy.

In the adult whose weight remains sensibly constant,
the indirect gain of energy from the environment is a
measure of the energy used for the maintenance of bodily

function and for the performance of external work. Certain features of the resting energy exchange under Australian conditions have been mentioned. So far no information is available as to whether the intake of additional energy for the performance of external work presents any special features under these conditions. No reason is known for supposing that the efficiency of the human machine under these conditions differs significantly from that found in experiments in more temperate climates. The existing data indicate that the total energy requirement of individuals at a given level of physical activity would be lower than in Europe or North America to an extent depending on the prevailing level of temperature.

Two groups of university workers, for example, who were examined in Sydney showed average daily intakes of Calories of 2 for men and 19 for women (Wardlaw, 1921, 1922). These figures are about 10 per cent. lower than average figures for corresponding European groups (Health Committee of League of Nations, 1936).

Determinations of the daily energy intake of Sydney schoolboys (Wardlaw and White, 1940) gave an average " man value " of 2,650 Calories per day. These figures differ to the same extent from the corresponding figures collected by the Committee cited, and also from those obtained by Friend (1935) on comparable English schoolboys. They also differ to the same extent from the figures arrived at by Cathcart and Murray (1931) as standards for the satisfactory nutrition of boys. They are rather lower than the similar figures recommended by the Committee on Nutrition of the British Medical Association (1933).

The figures used as " man values " for the comparison of energy intake of boys of different ages are those of Cathcart and Murray (loc. cit.). The actual total quantities of energy required depend on the size of the boys. The figures of Wardlaw and White (loc. cit.) indicate that the intake of materials the sole or principal function of which is to undergo oxidation with liberation of energy increases in proportion to the increase of surface area of the individual, illustrating in another way the close relation between energy exchange and external surface area. Certain other materials subserve other functions besides that of fuels. The intake of these materials (proteins and mineral constituents) appears to increase in proportion to the weight of the individual rather than to his surface area.

Examination of the distribution of the constituents of the diet which yield energy on combustion leads to one or two unexpected results. Australians are . commonly supposed to obtain an unusually high proportion of their energy from the combustion of protein. This supposition is based on statistics of meat consumption. These show that some years ago Australia had the highest meat consumption per head among civilised countries. Although the rate of meat consumption has fallen considerably since the last war, Australia is still among the high meat-consuming countries.

The diets of the groups of Australian adults and boys to which reference has been made do not show a proportion of energy derived from protein which is significantly different from that of corresponding European groups. The male adults examined obtained $17 \cdot 8$ per cent. of their total energy from protein, the boys, $14 \cdot 0$ per cent. It must be emphasized, however, that the figures available for Australians do not refer to manual workers. This section of the community is the most important in its effect on figures for total consumption both on account of the large proportion of the population which it forms, and because of the high rate of energy exchange of the group.

It has been indicated that under environmental conditions not uncommon in Australia a major problem of energy exch nge is to raise the rate of loss to a level high enough to balance the gain from the environment. The high calorigenic action of protein renders it obviously undesirable as a fuel under such conditions. Provided that the intake of protein is ample for the es ential function of this material, it is desirable that its use as fuel should be restricted as much as possible. This essential function has nothing directly to do with the production of energy in the body. The high meat consumption of Australians as a whole has probably been determined in the past by the relative cheapness of this class of food, and not by its physiological suitability to the conditions of life of the consumers.

Another unexpected observation is in the relative proportions of energy obtained by the combustion of fat and of carbohydrate. The proportion of fat in the diets of the Australian groups examined tends to be higher than that in the corresponding European groups. Yet it is generally supposed that the proportion of fat burned tends

to be higher in cooler climates. Here again economic
factors may have been preponderant. Fat is on the whole
a dearer source of energy than carbohydrate, and the
groups compared may not have been economically
comparable.

When strictly comparable groups are examined a
variation of the proportion of fat and carbohydrate used
is found to occur in the expected direction in respect to
the influence of external temperature. During the cooler
months of the year, for example, the Australian boys
referred to obtained a higher proportion of their energy
from fat than during the warmer months.

SUMMARY.

The exchange of energy between man and his environ-
ment occurs both directly (mainly as heat and mechanical
energy) and indirectly (as materials which react with
liberation or absorption of energy). Intake of "useful"
energy from the environment occurs only indirectly.

The disparity of rates of intake and of output of energy
under extreme conditions is discussed. The importance
of stores of material in the body for preserving the balance
between intake and output under such conditions is
indicated. The factors limiting rates of exchange and the
paths of exchange are considered. While direct exchange
can occur freely between the environment and the general
surface of the body in contact with it, indirect exchange is
limited to specific surfaces to which the environment has
not free access.

The relation between environmental temperature and
the distribution of indirect intake of energy appears to be
similar under Australian conditions to that found else-
where.

Under average conditions of temperature prevailing in
Australia the rate of intake of energy required for the
maintenance of the body in the resting state is lower than
that required under average conditions in Europe and
North America. Diminution of direct loss of energy
results in an economy of some 10 per cent. in the southern
and some 20 per cent. in the northern parts of Australia.
Diminution of direct loss (as distinct from direct gain)
can thus play a useful part in energy economy.

Under conditions of temperature frequently encountered
in Australia direct loss of heat from the body becomes
impossible. Direct gains may occur at rates as high as

that of the energy production of a man doing strenuous physical work. Under these conditions direct gain of energy from the environment is a serious embarrassment in the preservation of an energy balance. The whole burden of adjustment falls on the indirect loss of energy by evaporation of water. The importance of water exchange with the environment is emphasized, and some differences between aborigines and white inhabitants are indicated.

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STUDIES ON THE TUNG OIL TREE
(*ALEURITES FORDII* HEMSL.).

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1. INTRODUCTION.

The Tung Oil tree belongs to the genus *Aleurites* Forst. of the family Euphorbiaceæ. Six species of this genus are found in eastern Asia, Malaysia, and North Australia. The Tung is a native of southern and west-central China. In the central provinces, only one species, *A. Fordii* Hemsl., is found, but in the southern provinces of Kwangtung and Kwangsi three species are grown,[15] including, besides *A. Fordii*, *A. montana* (Lour.) Wilson, and *A. moluccana* Willd. *A. moluccana* is of recent introduction from Malaysia, and is grown for shade and not oil purposes. The other two species have been cultivated for their oil since antiquity, and reference is made to them in records of the Tang Dynasty (A.D. 618–906).

Of the two species, *A. montana* is sub-tropical and is cultivated in the most southern districts. *A. Fordii* requires a temperate climate such as obtains in the main Tung districts, and it is stated by Wilson[30] that this species is responsible for nine-tenths of the total Chinese production of tung oil.

Cultural Methods in China.

The cultivation of Tung in China has been described by several authors.[15, 21] Owing to its influence on the Tung stock, this system is worthy of note. The Tung is grown only as a minor crop, and its cultivation is restricted to the steep slopes in mountainous districts at elevations of up to 2,500 ft., where erosion is an important factor and the rainfall is a minimum of 30 inches per year. After the clearing of the land, corn, often with soya, is grown until profitable returns are no longer obtained. The Tung is then planted, usually *in situ*. It comes into bearing in from three to five years, depending on the variety, and remains productive up to the twelfth to twentieth year. The land is then allowed to revert to its natural state or is planted with pines, and after about twenty years it is cleared again for corn, and the rotation is repeated.

According to Hoh,[15a] no attempt at the improvement of Tung has been made in the thousand or more years of its known cultivation. Since the trees are monoecious and insect-pollinated, and since the two important species are apparently inter-fertile, it is to be expected that the whole Tung population of China is to a high degree heterozygous. This condition is indicated by Hoh,[15] who describes two distinct varieties of *A. Fordii* and indicates the occurrence of intermediates between these two extremes.

Description of Species.

The following much abbreviated descriptions of the two important species are taken from Hoh.

1. *A. Fordii* Hemsl., a tree, 3–12 metres high, without a central trunk. Stems drooping. Flowers appearing before leaves, on previous season's wood. Flowers in panicled cymes, chiefly staminate, terminal ones pistillate. Ovary woolly, three or more celled (usually five), stigmas bifid, styles four. Fruits smooth or slightly striate.

Variety " Three-year-Tung ". A small tree, three metres high. Crops in third year, and usually debilitated by

twelfth year. Fruits small, pendulous, in clusters of three or four to ten or more.

Variety " Five-year-Tung ". A tree 7–10 metres high. Crops in fifth year and remains productive for twenty years or more. Fruits large, usually solitary on short erect peduncles.

(2) *A. montana* (Lour.) Wilson. A tree, eight metres high, with a strong central trunk. Flowers borne on the current season's growth after the leaves have expanded. Pistillate and staminate flowers usually in separate clusters, staminate clusters many-flowered, pistillate clusters few-flowered. Ovary and fruit with three prominent ridges. Styles three, stigmas bifid. Seeds three.

A. Fordii is the species which has been most extensively grown in America, and it is the only one suitable to N.S.W. conditions, although *A. montana* can be grown in northern Queensland. From the studies herein described, it is evident that the material introduced to Australia is of mixed origin and probably heterozygous nature. By analogy with the results achieved with other crops, for example rubber, a very considerable improvement in Tung should be possible. For this improvement a great deal of work in selection and breeding is required, and only after this work has been tackled can the successful establishment of the industry be assured.

2. The Material.

It is difficult to trace the exact source of all the Tung trees now growing in Australia. The first introduction of seed was obtained from the Royal Botanic Gardens, Kew, in 1911, and this seed was planted at the Botanic Gardens, Sydney.[29] Only one seed germinated, and this tree was grown at the Gardens. In 1920 seed from this tree was distributed to Grafton, Wollongbar, and elsewhere.[26]

In 1927 seed was obtained by Kew from Florida, U.S.A., and some of this seed was distributed in Queensland and in New South Wales.[1, 9] At the same time Kew also distributed seed obtained directly from China.[1, 3] About the year 1926, also, Whittell apparently brought seed direct from China. Further introductions of seed were made from Florida as late as 1931.

The Tung groves which have been studied in this paper comprise portion of a plantation owned by Mr. A. H.

Woolcott at Bargo, and include stock of several origins, namely :

(a) "*Bundanoon* " *stock*.   These trees are derived from a plantation at Bundanoon, and are of mixed origin. They include trees derived from Florida seed as well as trees of Pennant Hills and Grafton origin.   They consist of a block of less than 200 trees which were planted in 1933.

(b) "*Pennant Hills* " *stock*.   These are reputedly derived from seed obtained by Whittell from Hankow, China, in 1926, which was planted at Pennant Hills.   The group consists of a block of about 200 trees of the same age as the Bundanoon trees.

(c) "*Grafton* " *stock*.   Derived from two good-yielding trees at Grafton, New South Wales, which in turn were derived from the original Botanic Gardens tree.   The group comprises several age classes, planted in 1934 and subsequently, and constitutes the greater part of the Bargo plantations.

(d) "*Local* " *stock*.   In addition to the above groups there are a number of blocks of young trees, planted in 1937 and 1938, derived from individual, high-yielding trees of the first two groups, which should provide valuable material for future studies.

The studies herein described concern chiefly the Bundanoon and Pennant Hills blocks.   The general cultural system adopted with the young trees is clean cultivation, combined with the growth of a green manure or fodder crop between the rows.   Oats may be grown, partially fed off with sheep, and the residue ploughed in. The ultimate aim is to put down a permanent pasture between the trees.   The only pruning adopted consists in the removal of dead wood and in the rubbing off of shoots which arise low down on the main stem.   Any other attempt at shaping the trees is not favoured, and pruning is considered undesirable.   Where pruning has been adopted the soft pithy wood has been found to rot rapidly often to the base of the tree.   One block of Grafton trees planted in 1934 has been left entirely unpruned.

3. General Yields.

Climate and Yield.

The climate at Bargo, with an average rainfall of 29 inches, and with a wide range in seasonal and diurnal temperatures, would not normally be considered a suitable

district for Tung cultivation. Climatic data for Bargo are compared with data for the Tung districts in Florida in Table 1.

Wilson[30] has described the ·climatic conditions under which Tung is grown in China, and several authors[1, 16] have made reference to the desirable conditions. Briefly these are a minimum rainfall of 30 inches and preferably 50–70 inches, suitably distributed, absence of severe late frosts and warm but not excessive summer temperatures. These requirements are hardly fulfilled at Bargo, and it is not surprising that the general average yields have been low, even for young trees, and that even the best trees have not given yields equal to some obtained in better rainfall districts.

Abbott[6] has studied the effect of soil moisture conditions on the development of flower-bud initials of Tung in America. Excessive moisture so delays the formation of these initials that their proper development is not possible by the normal flowering season, and it also adversely influences the development and maturation of the fruit.[7] On the other hand, drought conditions and high temperatures such as have been experienced at Bargo cause a cessation of normal vegetative growth and consequent early production of flower initials. Such conditions also result in a reduced number of flower initials on the restricted wood growth, and consequently in the subsequent year's crop. This has evidently been the case at Bargo for the coming 1939–40 season as shown by flower counts, which indicate a poor prospective crop.

The effect of drought and heat is also apparent in the average size of fruit. The exceptionally dry 1939 season has resulted in fruit of little more than half the normal average weight. The development of the kernels has also been affected by these conditions.

It has been stated[1, 3, 15, 24, 30] that Tung is able to withstand only mild frosts during the growing season. Frosts at time of flowering (October at Bargo) are likely to cause even more· damage. Although Bargo, with an elevation of 1,118 feet, is subject to late frosts and cannot be considered a safe district, none have been experienced during the past two seasons. Temperatures as low as 4° F. may be endured by Tung during the dormant season.[30]

The growth and yield of the more exposed trees in the plantation have shown the necessity for effective wind

TABLE 1.

Comparison of Mean Monthly Rainfall and Temperature Data for Picton,* New South Wales, and Gainesville, Florida.

Picton.	Jan.	Feb.	Mar.	Apr.	May.	June.	July.	Aug.	Sept.	Oct.	Nov.	Dec.	Year.
Mean rainfall for the two years 1938 and 1939	2·95	1 32	2·95	1 76	1·71	0 53	0·83	4 65	1·13	3 01	2·60	0 55	23 99
Mean monthly temperatures, 1938 and 1939, ° F.	74 5	74·0	70·3	63·1	57 5	49·5	46 5	51·5	55 7	62 8	68·4	71·9	62·15

Gainesville, Florida.	July.	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May.	June.	Year.
Mean rainfall, in inches	7 32	6·76	5 65	2 84	2 04	3 22	3 31	2 87	3 21	2 21	3 11	6·57	49·11
Mean monthly temperatures, ° F.	80·4	80 8	79·0	72·3	62·5	58 2	57 8	58 4	63·7	69 3	75 0	79 3	69·7

* Picton, twelve miles from Bargo, is the nearest Meteorological station.

breaks.   Winds of gale force were experienced in December,
1938, and, although a few trees were destroyed, little
obvious damage was done and practically no fruit was lost.
A more serious effect is evident with those trees exposed
to prevailing winds.   Yields from such trees are invariably
low, growth is poor, and the trees bear a straggly and lean
appearance.

Average Yields.

It has been variously stated[15, 21, 24] that the Tung tree
commences to bear fruit at from 3–5 years of age, and that
it reaches full.bearing at from 8–10 years.   The trees
studied at Bargo have yet to attain their maximum
productivity.   It has been stated (Penfold) that yields
averaging 1,000 fruits per tree from mature trees are
necessary for profitable production, although whether
returns are payable or not will depend upon many economic
factors, such as the cost of the land, prices of the oil, and
cultural methods, such as the simultaneous use of the land
for pasture.   Although the average yields at Bargo cannot
be expected to approach 1,000 per tree even after maturity,
they must be considered fairly satisfactory in view of the
not altogether favourable climatic conditions and the high
proportion of low-yielding trees.   The indications are that,
provided selected and improved stock only is planted,
profitable crops can be expected in the district.

At Bargo two-year-old trees only very occasionally bear
a few fruit.   The average yield from a block of 103 three-
year-old trees of Grafton origin in 1938–39 was 14·7 fruits
per tree.

The yields from Bundanoon and Pennant Hills blocks
for the seasons 1937–38 and 1938–9, when the trees were
four and five years of age respectively, are shown in
Table 2.

TABLE 2.
Average Yields of Fruit.

Group.	No. of Trees.	Average Yield 1937–1938. Trees 4 Years.	Average Yield 1938–1939. Trees 5 Years.	Percentage Increase.
Bundanoon ..	176	47·5	166·0	349·4
Pennant Hills ..	196	55·8	169·0	302·8
Total ..	372	51·9	167·5	322·7

No real or significant difference is shown between the two groups, and the percentage increase for the second year is satisfactory in both cases. The average yields given include those from a number of trees situated in, and badly affected by, low-lying, badly drained pockets, and in the case of the Bundanoon group of a number of inherently low-yielding types which could be easily culled. Considerably higher average yields for the fourth and fifth years should thus be easily obtained.

4. Variation Studies in Tung.

Owing to the monoecious character and cross pollinated habit of the Tung Oil tree, and its unimproved condition and mixed origin, it is not surprising to find a considerable degree of variation amongst any group of trees. Although numerous authors[1, 7, 15, 21, 22, 24] have referred to this variation, the only detailed study is that of Mowry,[22] based on 23 trees of the Florida Agricultural Experiment Station. This paper deals with variations in yield, fruit size and shape, and proportion of kernel in the fruit.

Variation in Vegetative Characters.

Heavy yield of oil is the ultimate criterion of the value of a tree. Other factors which may have an indirect bearing on the yield, or upon the care and management of the trees, are also worthy of study.

Vigour. Trees among all groups at Bargo show very pronounced differences in vigour. Among the Bundanoon and Pennant Hills groups the height of the trees varies from six feet to almost twenty feet. It is obviously impossible to determine the proportion of such differences due to environmental conditions and that due to inherent factors. Whilst many of the weakest trees are suffering from adverse soil conditions, such as obtain in several well-defined low-lying and badly drained patches, much of the variation would appear to be inherent. This is indicated by the much greater variability of the Bundanoon group of mixed origin as compared with the Pennant Hills and Grafton groups. It will be shown later that in the Bundanoon group lack of vigour is apparently correlated to some extent with the " umbrella " habit, and, naturally, with low yields. Definite correlations with other characters could not be demonstrated.

Habit. The " Pennant Hills " and " Grafton " groups are of surprisingly uniform habit of growth. The general form of these trees is the possession of a central trunk, with a whorl of 5–7 branches at a height of 3–4 feet, and a second whorl of 3–4 branches at an interval of 3–5 feet. The lateral branches ascend at an angle of about 30° in the lower half, and, except when laden with fruit, are more erect in the upper half.

The trees of one block, derived from Grafton seed, which have been allowed to grow wild, show a number of water-shoot growths from the base of the trees, but otherwise resemble the other " Grafton " trees in appearance. Among the " Bundanoon " trees, however, several quite distinct habits are to be seen. The " Pennant Hills " or " Normal " type just described is well represented, but the following habit types are also found :

(*a*) *The " Bush Head " type.* The whorled arrangement of lateral branches from a central trunk is not evident, the main stem branching irregularly. The main branches droop noticeably, and bear flowering spurs along their whole length, in marked contrast to the normal type. The type appears to be restricted to trees of single fruiting nature, and the single fruiting habit is counterbalanced by the large number of flowering spurs produced. It usually bears fruit of large size and the fruit characters resemble those of the " Five-year-Tung " variety of Hoh.

(*b*) *The " Umbrella " type.* In these trees the central trunk ascends to a height of five to eight feet before branching. It is then surmounted by a small parasol-shaped head. The trees are usually of poor vigour and low yield. This type is not found other than in the Bundanoon block.

(*c*) *The " Pine " type.* In this type the lateral branches arise from the main trunk uniformly along its length, not being whorled as in the normal habit. As a type it is likely to be resistant to wind damage, but it does not appear to be definitely correlated with other important characters.

(*d*) *The " Low-branching " type.* In this type there is no trunk, and the trees tend to branch very low to the ground, the main branches growing out almost horizontally. The type is very susceptible to wind damage, and is undesirable.

Among the 176 trees of the Bundanoon group the types were distributed as follows :

" Normal " type	..	..	..	81
" Umbrella " type ..	..	..	..	40
" Bush Head " type	..	..	..	18
" Pine " type	..	..	..	13
" Low Branching " type	..	..	..	4
Indeterminate	..	..	..	20

176

The indeterminate trees are those which have made such poor growth, due to badly drained situations, that their inclusion in any of the above groups is not practicable.

The several blocks of Tung trees show variations in such vegetative characters as leaf, shape and size, and the position of the leaf glands, etc., but these have not been studied.

Variation in Flowering Characters.

Among the most obvious variations in Tung are those affecting the flowering characters of the tree. Differences of up to two weeks in the dates of first flowering between adjacent trees are frequent. Abbott[6] has shown that seasonal conditions may have an important effect on flower development, but the differences noted at Bargo do not appear to be environmental. In some trees the habit of *A. montana*, in which the flowering follows the expanding of the leaves, is approached.

Mowry,[22] Newell *et al.*[25] and others have noted that the proportion of staminate flowers appears to vary considerably between different trees. Abbott[6] has noted that four-year-old trees have a higher proportion of pistillate flowers than older trees. It has been noted at Bargo that the proportion of staminate flowers appears to be dependent upon weather conditions, the age of the trees, and their genetic constitutions.

Weather conditions have a very important influence upon flower bud initiation,[6] and from observations in October, 1939, it would appear that dry or droughty conditions during the summer and autumn reduce not only the total number of flowers but also the proportion of staminate flowers in the following blossoming seasons. Sufficient data are not yet available for a full study of this factor.

The results of flower counts over two years at Bargo indicate that the proportion of the staminate flowers increases with age. Two-year-old trees only occasionally produce flowers, but all such flowers examined have been pistillate. Apparently no staminate flowers are produced at this age. In three-year-old trees staminate flowers are scarce and frequently absent. In four-year-old trees only an average of 25 per cent. of the flowers appear to be staminate, although considerable differences occur between individual trees. In later years this proportion may increase to 60–80 per cent. or considerably higher. The figures in Table 3 show the proportions of staminate flowers on selected trees for the blossoming periods October, 1938, and October, 1939. To eliminate the interference of seasonal effects further records are necessary on the relation of age and flowering habits.

TABLE 3.

Increase of Staminate Flowers with Age.

Group.	No. of Trees.	Percentage Staminate Flowers, 1938.	Percentage Staminate Flowers, 1939.
Bundanoon, planted 1933 ..	6	82·7	81·0
Pennant Hills, planted 1933	5	60·9	74·0
Grafton, planted 1934 ..	7	26·1	61·1

In the case of all groups, but particularly in the Bundanoon group, highly significant differences were found in the proportion of staminate flowers on different trees in the season October, 1938. In selecting trees for the counts given a random selection was not made, but a selection was made to show the range of extreme types as well as intermediate types.

Tables 4 and 5 show the degree of variation which may occur in the proportion of staminate flowers. In a tree such as $3/10$–20, the flower clusters are large and contain numerous flowers or buds, usually from forty to sixty, but sometimes eighty or more, with rarely more than one pistillate flower in the whole cluster, and even that frequently imperfectly developed. On this particular tree in the 1938 season it was estimated that there were 8,000–10,000 flowers, of which only about 100 were pistillate. Trees of this type are apparently referred to by Mowry[22] in his study of variation in Tung in Florida.

TABLE 4.

Proportion of Staminate Flowers, Individual Trees.
Paddock 7. Four years old Grafton trees, 1938.

Row and Tree.	Clusters.	Pistillate Flowers.	Staminate Flowers.	Percentage Staminate Flowers.
5— 9	10	60	13	17·8
5—10	10	70	36	34·0
4—11	10	60	4	6·25
3—22	10	44	0	0·00
6—22	9	45	11	19·6
8—18	10	37	59	61·5

TABLE 5.

Proportion of Staminate Flowers, Individual Trees.
Paddock 3. Five year old trees.

Row and Tree.	Group.	Clusters.	Pistillate Flowers.	Staminate Flowers.	Percentage Staminate Flowers.
4—20	Bundanoon	10	47	209	81 6
6— 8	′ ,,	10	41	136	76 8
6—10	,,	5	24	76	76·0
7—10	,,	9	37	112	75·1
10—20	,,	5	3	254	98·8
11—19	Pennant Hills	10	32	87	73 1
19— 9	,,	10	57	44	43 6
19—18	,,	10	50	76	60 5
20—11	,,	10	42	80	65·6

The opposite type is shown in trees such as ³/19–9, in which less than half the flowers are staminate. In such trees the clusters consist usually of less than ten flowers, of which as many as five or even more may be pistillate.

A less conspicuous but equally important variation is shown in the number of pistillate flowers (and consequently also fruits) per cluster among trees which do not conform to the male type. This type of variation has been noted in Australia by Penfold and Morrison[27] and by Cheel, in America by Newell,[24] Mowry[22] and others, by Hill in England, and by Hoh[15] in China. Among the trees at Bargo the following types are distinguishable :

(a) *The single fruiting type.* The flower clusters are small, usually consisting of only one, occasionally of two or three pistillate flowers, with the lateral staminate flowers more or less completely suppressed, and only occasionally well developed. The pedicels are short and erect and the

trees are invariably of the " dense head " habit.   The type
closely agrees with the " five-year-tung " variety described
by Hoh.

(b) *The large cluster or " Florida " type.*   The clusters
contain often five and sometimes as many as nine or ten
pistillate flowers with rather more staminate flowers.   The
fruits are developed on long pendulous pedicels and are
frequently of small size.   The type has been described
by Mowry[22] and has been universally favoured in America,
Australia,[19] and elsewhere ; it is typical of the Grafton
and Pennant Hills blocks.   In some respects the type
resembles the " three-year-Tung " variety described by
Hoh, and may not be as desirable a type as has been
assumed.

(c) *Intermediate types.*   Types intermediate between the
two above are of frequent occurrence in the Bundanoon
block.   The number of pistillate flowers varies from one
or two to five or six per cluster, and such intermediates
may approach closely to either extreme.   Under adverse
weather conditions the number of pistillate flowers per
cluster in trees of the large cluster type might be very
considerably reduced, and intermediate types cannot
consequently be exactly defined.

The numbers of trees of the different flowering types in
the Bundanoon block are :

Single fruit	18
Intermediate type	88
Large cluster type	24
" Male " type	9
Indeterminate type	37

The indeterminate trees could not be placed in any group
on account of low yield due to unfavourable conditions.

The occurrence of flower abnormalities has been noted
in a number of trees.   In the tree ³/10–20, already men-
tioned, and in some other trees, flowers with both stamens
and pistil were found, an occurrence already noted by
Mowry[22] in Florida.   Such flowers are usually deformed or
poorly developed and would fail to set, or would produce
only small and malformed fruit.   By their terminal
positions in the clusters they are apparently equivalent to
the normal pistillate flowers.

Another abnormality noted, particularly in the Grafton
trees, is the occurrence of empty flowers, without pistil
or stamens, but with perfectly developed corolla.   In

the case of one tree approximately 15 per cent. of the terminal flowers of the clusters were thus empty.

In the case of the single-fruiting type, found among the Bundanoon group, suppressed lateral staminate flowers, with a barely developed or a quite undeveloped corolla but with considerable pollen are found. The search for these was suggested by Hill, but they are distinctly rare and appear to be produced too late to be of any importance in pollination.

Variation in Yield Factors.

The final criterion in the evaluation of Tung trees is the total production and quality of the oil. For the purpose of field study, yield may be divided into a number of factors, viz: number of fruits per tree, size of fruit, proportion of kernel to husk, and oil content of the kernel. An attempt has been made to study these factors separately at Bargo, and although they are subject to climatic and other environmental conditions, the degree of variations and the nature of the correlations noted indicate an important measure of inherent differences.

Number of Fruits per Tree. Yields of fruit from individual Tung trees have occasionally been very high. Under favourable conditions such yields have been recorded exceeding 1,500 fruits, but the average yield from whole plantations have usually been disappointing.

A block of trees of Grafton origin, planted in 1935, has been already quoted as averaging 14·67 fruits per tree in the 1938–39 season, when three years old. Yields from individual trees, however, varied from zero to 109 per tree, the yield distribution, as shown in Table 6, indicating that only an occasional tree gives an appreciable yield at this age.

TABLE 6.

Yields of Three-year-old Tung Trees.
Paddock No. 1.   Grafton origin.

Yield Group. No. of Fruits per Tree.	No. of Trees.	Yield Group. No. of Fruits per Tree.	No. of Trees.
0–9	70	60–69	2
10–19	12	70–79	2
20–29	5	80–89	2
30–39	2	90–99	1
40–49	1	100–109	1
50–59	5		

Total : 103.

The paddock is an isolated small block, well protected from winds, and situated on level ground. The soil appears to be uniform, and could scarcely account for the degree of variation found.

It does not necessarily follow that trees yielding high in their third year are desirable, or that they will prove the best yielders ultimately.

The distribution by yield groups for the Bundanoon and Pennant Hills blocks, planted in 1933, for the seasons 1937–38 and 1938–39, are given in Table 7. The large number of trees in the low-yield groups is partially explained by the inclusion of trees affected by badly drained situations, and partly by the occurrence of a large number of inherently inferior types.

TABLE 7.
Yields of Four- and Five-year-old Tung Trees.
Paddock No. 3. Planted 1933.

1937–38 Season.			1938–39 Season.		
Yield Group. No. of Fruits per Tree.	Bundanoon. No. of Trees.	Pennant Hills. No. of Trees.	Yield Group. No. of Fruits per Tree.	Bundanoon. No. of Trees.	Pennant Hills. No. of Trees.
0–19	66	82	0–49	41	35
20–39	39	24	50–99	22	30
40–59	17	16	100–149	21	37
60–79	17	14	150–199	26	18
80–99	11	15	200–249	23	24
100–119	10	15	250–299	17	19
120–139	5	9	300–349	12	18
140–159	5	6	350–399	7	10
160–179	2	8	400–449	2	3
180–199	2	2	450–499	1	1
200–219	1	2	500–549	2	1
240–259	—	1	550–599	2	—
280–299	—	1			
320–339	—	1			
420–439	1	—			

A high correlation exists between the yields of the two years, showing that a similar set of controlling factors was operative. This correlation is shown in Table 8, the most notable features being the continued low yield of the poorer trees and the relatively high average yields of the top groups.

In connection with this table, it should be noted that records in Florida[23, 24, 25] indicate that the high yielding ability of individual trees is maintained over a number of years.

TABLE 8.

Correlations of Yields.

Average Yields, 1938-39, of 1937-38 Yield Groups.

Mean Yield Group, 1937-38. No. of Fruits.	No. of Trees.	Average Yield, 1938-39.	Mean Yield. Group. 1937-38. No. of Fruits.	No. of Trees.	Average Yield, 1938-39.
Over 190	10	345·7	70-79	15	223·0
170-189	8	369·0	60-69	15	223·1
150-169	8	324·0	50-59	17	212·6
130-149	9	306·2	40-49	16	192·1
120-129	11	284·0	30-39	22	200·0
110-119	9	293·0	20-29	41	141·4
100-109	16	244·0	10-19	47	107·9
90-99	12	283·5	0-9	102	48·0
80-89	14	257·5			

Total number of trees : 372.   Average yield, 1938-39 : 167·5.

A strong correlation would be expected between yield and vigour, and such was generally found to be the case ; the lack of vigour was due to obvious unsatisfactory conditions or to more obscure inherent causes.   A correlation between yield and habit growth, however, appeared to be independent of environmental conditions.   It has been explained that the trees have not been pruned, and the habit of growth adopted by each tree may be taken as an indication of its natural inclination.   In Table 9 it will be seen that the most definite and significant correlation is that of low yield with the " umbrella " type.   This table deals only with the Bundanoon group, which alone shows appreciable difference in habit.   The correlation of the " Pine " habit and yield is doubtful, and insufficient of the " low-branching " type occur for an indication to be obtained.   The occurrence of the " umbrella " type scattered at random throughout the block would appear to be largely dependent on hereditary factors.

In Table 10 the correlation of yield with fruiting type is shown.   The only positive correlation indicated is between the " male " type and low yield, although insufficient numbers of the type occur for definite conclusions to be drawn.

The important conclusion to be drawn from the results is that the single-fruiting type has a potential yielding ability equal to that of the cluster type, which latter has been universally favoured by growers both in America and Australia.   The large numbers of fruiting spurs produced by the single type balances the advantage of the cluster type in number of fruits per cluster.

TABLE 9.

Correlation of Yield and Habit.
Bundanoon Block, 1938–39.

Number of Trees in each Group.

Yield Group.	" Normal."	" Umbrella."	" Bush Head."	" Pine."	Low Branching.	Indeterminate.	Total.
0–49	3	16	—	1	1	20	41
50–99	7	13	—	1	1	—	22
100–149	10	7	—	3	1	—	21
150–199	15	4	4	3	--	—	26
200–249	16	—	6	--	1	—	23
250–299	13	--	2	2	—	—	17
300–349	7	—	4	1	—	—	12
350–399	5	—	—	2	—	—	7
400–449	2	—	—	—	—	—	2
450–499	1	—	—	—	—	—	1
500–549	1	—	1	—	—	—	2
550–599	1	—	1	—	—	—	2
Totals ..	81	40	18	13	4	20	176

NOTE.—" Indeterminate " trees are trees which could not be grouped on account of poor growth due to unfavourable soil conditions.

TABLE 10.

Correlation of Yield and Fruiting Type
Bundanoon Block, 1938–39.

Number of Trees in Groups.

Yield Group.	Single Fruiting.	Intermediate.	Cluster.	Male.	Indeterminate.	Totals.
0–49	—	3	—	1	37	41
50–99	--	17	3	2	—	22
100–149	—	18	1	2	—	21
150–199	4	20	1	1	—	26
200–249	6	10	5	2	—	23
250–299	2	11	3	1	—	17
300–349	4	3	5	—	—	12
350–399	—	3	4	—	—	7
400–449	—	1	1	—	—	2
450–499	—	1	—	—	—	1
500–549	1	—	1	—	—	2
550–599	1	1	—	—	—	2
Totals ..	18	88	24	9	37	176

NOTE.—" Indeterminate " trees are those which could not be grouped owing to poor yield due to unfavourable soil conditions.

Variation in Size. Mowry[22] has described the occurrence of differences in both size and shape between the fruit of different trees. The average size of the fruit

at Bargo in the 1939 season was exceptionally small, owing presumably to the drought conditions experienced. However, considerable differences occurred between the fruit of individual trees, ranging from fruits barely larger than marbles to fruits of reasonable size, weighing 20–25 grams air dry. From Table 12 it will be seen that the actual yield of kernel per fruit may be three times as much for some as for others, and that the smaller fruits had a low proportion of kernel.

An apparent correlation between the size of the fruit and the number carried by the tree was noted both in the case of the Bundanoon and Pennant Hills groups, but records were kept in the case of only a few trees. Such a correlation would be expected on physiological grounds, and would not require any genetic explanation. An interesting correlation appears to be likely between size and fruiting type, the single-fruiting type tending to produce the larger fruit. If such a correlation is definitely established, it will seriously effect the desirability of the cluster type. A table compiled from notes on only the higher yielding trees of the Bundanoon block (Table 11) indicates approximately this correlation.

TABLE 11.

Correlation of Fruit Size and Fruiting Habit.
Bundanoon trees. Paddock 3. 1938–39.

Number of Trees in Groups.

Size.	Single Fruiting.	Intermediate.	Cluster.	Totals
Very small	—	1	3	4
Small	1	7	9	17
Average	1	14	6	21
Fair	5	6	2	13
Large	5	2	—	7
Totals	12	30	20	62

Trees yielding over 100 fruits in 1937–38, or over 230 fruits in 1938–39 only included.

Variation in Kernel Proportions. Mowry[22] has noted variations in the proportion of kernel and husk in the fruit of different trees, and various analyses of bulk samples of fruit from different countries by Jordan[17] and others have shown proportions of kernel ranging from 28 to 35 per cent. Such differences are of considerable importance,

and although they may be due to differences in climate, they may also be due in part to genetic factors. In Table 12 there are given the results of the analyses of samples of fruit from six trees of the Bundanoon and Pennant Hills blocks, the trees being selected for this study on the basis of other characters.

TABLE 12.

Analyses of Fruit Samples.

Tree.	Type.	Average Weight. of Fruit (Air-dry). Grams.	Percentage Calculated on Air-dry Whole Fruits.			Percentage Calculated on Weight of Kernels.	
			Outer Husk.	Seed Coat.	White Kernel.	Moisture.	Oil.
19–17	Cl	14·95	61·51	22·94	15·55	4·5	40·6
20–11	Cl	16·94	50·65	26·92	22·43	4·6	48·3
7–10	Cl	18·66	41·31	24·49	34·20	3·5	58·4
8–18	Cl	18·78	46·61	25·56	27·83	3·7	52·4
10–1	S	20·02	54·67	19·96	25·37	4·2	51·0
4–3	S	21·83	43·37	23·71	32·92	6·0	52·6

Compared with the results obtained by Mowry in Florida, these figures show a high proportion of husk. Mowry found that a high proportion of kernel was correlated with large fruit size, and the few results given here are not entirely contrary to this view. In the case of the smallest fruits the kernel was found to be dry and shrivelled, while in the larger fruit samples the kernels were plump and oily to the touch.

Variation in Oil Content. The figures given in Table 12 show a variation in the oil content of the kernel from 40·6 to 58·4 per cent. Penfold and Morrison[27] have given figures for the oil content of bulk samples from different sources varying from below 40 to over 65 per cent. Such differences are likely to be important, and more extensive work is required to determine the range of variation as affected by both environmental and internal characters.

From the results outlined in the foregoing section of this paper the Tung oil tree is seen to show, if not exceptional, at least very considerable variation in many of its important characters. The number or weight of fruit per tree is probably the most important single yield factor, but proportion of kernel and of oil cannot be neglected. It is

hoped to continue the study to obtain a more exact knowledge of variation in Tung, but sufficient is known to indicate the great possibilities offered in the improvement of the trees and the necessity for this if Tung oil is to become an established industry in Australia.

5. Pollination Studies.

The monoecious nature of the Tung tree has already been described, and the great variations which occur in the proportion of pistillate and staminate flowers has been shown, trees occasionally being almost dioecious. The pollen is of a sticky nature, suited to transference by insects, but quite unsuited to wind dissemination. Both pistillate and staminate flowers produce considerable quantities of nectar, and attract numerous ants and other small insects, besides bees and larger insects. The structure of the flowers is such as to suit pollination by large insects, bees and the larger wasps being effective, whereas smaller insects are useless.

At Bargo the first opening of the flowers occurs during the first week of October and continues for about three to four weeks thereafter, although odd flowers can be found well into November. Considerable difference occurs in the date of flowering of different trees, and this difference may be as much as two or even three weeks. Such a difference is likely to be of some importance with regard to the occurrence of late frosts, and it means that in a grove pollen is usually available over an extended period. With normal pollination the pistillate flowers usually remain open for from four to five days before commencing to wither. The staminate flowers usually fall more rapidly. In any one cluster, except in the male type trees, the staminate flowers usually open after the terminal pistillate flowers.

Of the effective insects which have been noted visiting the flowers, the ordinary bee is most numerous. On a bright day bees have been seen actively working on the flowers and frequently travelling from one tree to another. Other effective insects which have been observed are wasps of the families Thynnidæ and Scoliidæ. Non-effective insects seen visiting flowers included ants, hover-flies (Bombyliidæ) and numerous small and minute Diptera.

Natural Set Studies.

In order to determine the sufficiency of available pollen, and the effectiveness of pollination, fruit-set counts were made on a number of trees in the 1938 season. In two-year-old trees the few flowers observed have been invariably pistillate, and in three-year-old trees the proportion of pistillate flowers is very low, although actual counts have not been made on trees of this age. The fact that the pistillate flowers on two-year trees usually set led to a suspicion of parthenocarpy. In the case of four- and five-year-old trees, fruit set counts were obtained in conjunction with the flower counts given in Tables 4 and 5 on page 53. These results are given in Tables 13 and 14.

TABLE 13.
Fruit Set under Normal Conditions.
Paddock 7. Four-year-old Grafton trees. 1938–39.

Row and Tree.	Clusters.	Percentage Staminate Flowers.	Number Pistillate Flowers.	Fruit Set.	Percentage Fruit Set.
5—9	10	17·8	60	21	35·0
5—10	10	34·0	70	46	65·7
4—11	10	6·25	60	19	31·7
3—22	10	0·00	44	17	38·5
6—22	9	19·6	45	27	60·0
8—18	10	61·5	37	29	78·4
Totals ..	59	28·0	316	159	50·3

TABLE 14.
Fruit Set under Natural Conditions.
Paddock 3. Five-year-old trees.

Row and Tree.	Group.	Clusters.	Percentage Staminate Flowers.	Pistillate Flowers.	Fruit Set.	Percentage Fruit Set.
4—20	Bundanoon.	10	81·6	47	22	46·8
6—8	,,	10	76·8	41	38	92·7
6—10	,,	5	76·0	24	24	100·0
7—10	,,	9	75·1	37	37	100·0
10—20	,,	5	98·8	3	1	33·3
11—19	Pennant Hills.	10	73·1	32	29	90·6
19—9	,,	10	43·6	57	53	93·0
19—18	,,	10	60·5	50	47	94·0
20—11	,,	10	65·6	42	41	97·6
Totals	.. ..	79	76·4	333	292	87·7

The Grafton trees are all of the cluster type, and are uniform in habit of growth. Considerable variation exists in the proportion of staminate flowers on different trees, and this proportion is often low. The percentage of fruit set is also low, when compared with the results given in Table 4, for five-year-old trees ; moreover it is roughly proportional to the percentage of staminate flowers, thus indicating a relation between abundance of pollen and fruit-set. The transference of pollen from one tree to another is indicated by the setting of fruit on tree 3–22, which had a marked scarcity or absence of staminate flowers.

Similar counts for five-year-old trees are given in Table 14. A much higher proportion of staminate flowers is found, and except in the " male " type trees in which the few pistillate flowers are frequently malformed, the percentage fruit-set approaches, or may even reach 100 per cent. A general abundance and sufficiency of pollen is evident, and where individual trees such as 19–9 produce only few staminate flowers, this is balanced by the abundance of pollen from adjacent trees.

Parthenocarpic Fruit Development.

Owing to the suspicion of parthenocarpy which has been mentioned, a number of clusters on four-year-old trees were covered with glacine bags after the removal of all staminate buds and all pistillate buds except the terminal well developed buds which could be expected to open within a week, on 5th October, 1939. On the 11th October the bags were adjusted to allow room for the developing clusters, and in half of the clusters the flowers were pollinated by hand. The bags were removed on the 26th October. The results, which are summarised in Table 15, indicate that under the conditions of high temperature and humidity induced by the bags, no fruit setting will occur without pollination.

Of the flowers bagged but not pollinated, many were still attached on the 26th October, when the bags were finally removed. They had shown very little development, however, and all had fallen by the 25th November.

In order to eliminate any effects caused by the glacine bags in the previous experiment, and to determine the importance of insects in Tung pollination, four trees were enclosed in large frames covered with muslin, and made to exclude any but extremely minute insects. In each case,

TABLE 15.
Results of Bagging Experiment.
Paddock 1. Four-year-old Grafton trees.
October, 1939.

No. of Clusters Bagged.	No. of Flowers.	Date Bagged.	Treatment. 11th Oct.	No. of Young Fruit still Attached.		Diameter of Fruit.
				26th Oct.	25th Nov.	
16	16	5th Oct.	Pollinated.	14	10*	$\frac{1}{4}-\frac{3}{8}$ in. on 25th Nov.
16	22	5th Oct.	Not pollinated.	16	0	—

* $71 \cdot 4\%$.

one branch was left exposed outside the cage to serve as a control. The results of fruit-set counts on these trees are given in Table 16. In the case of the two Bundanoon trees, owing to the lateness of caging, many pistillate flowers opened and had to be removed, and many staminate flowers had fallen. Consequently the percentage of staminate flowers given for these trees is very low.

From the results, it is evident that insects are necessary for the pollination of Tung. In all of the caged trees a considerable proportion of the fruit was still attached six weeks after ageing, and a slight amount of wind pollination, insufficient to provide the physiological stimulus necessary for proper fruit development, was at first suspected. During the following month, however, all this fruit had fallen, and it is probable that the conditions inside the cages, which provide protection from wind and strong sunlight, simply favoured the partial development of the unpollinated fruit.

Pollen Distribution.

A number of experiments were carried out during October, 1939, in an attempt to determine the extent of pollen distribution. In a block of four-year-old Grafton trees, all staminate flowers were removed from certain trees immediately prior to flowering, and with other trees the staminate flowers were removed from one half of the tree. The results of this work are given in Table 17, together with counts of normal fruit-setting made at the same time. It is evident that, where the number of staminate flowers on a tree is deficient, this deficiency may be made up from pollen from adjacent trees. Trees

TABLE 16.

Fruit Sets in Caged Tung Trees, 1939.

Tree.

	Grafton. 4 years. 5th Oct. 38·8		Grafton. 4 years. 5th Oct. 76·8		Bundanoon. 6 years. 18th Oct. 25·0*		Bundanoon. 6 years. 18th Oct. 32·6*	
Origin								
Age								
Date caged								
Ordinary percentage staminate flowers								

Treatment.

	Caged Staminate Flowers Removed.	Exposed Staminate Flowers Left.	Caged Staminate Flowers Left on.	Exposed.	Caged Staminate Flowers Left on.	Exposed.	Caged Staminate Flowers Removed.	Exposed Staminate Flowers Left.
No. of pistillate flowers left	46	17	24	4	48	5	99	11
No. of fruit attached 25.11.39	36	16	15	4	4	4	32	10
Diameter of fruit 25.11.39	Under ¾″	1¼″–1½″	under ½″	1¼″	under ½″	1″–1½″	¼″–½″	1¼″–1½″
No. of fruit attached 22.12.39	0	12	0	4	0	4	0	9
Percentage of fruit set	0	75	0	100	0	80	0	81·8

* Many staminate flowers fallen. Percentage figure low.

TABLE 17.

Fruit Set Studies. Staminate Flowers Removed.

Paddock 1. Four-year-old Grafton trees.

Tree.	Treatment.	Clusters.	No. of Pistillate Flowers.	No. of Staminate Flowers.	Percentage Staminate Flowers.	No. of Fruit Set.	Percentage Fruit Set.
3—5	All staminate flowers removed	14	17	0	0	13	76·4
4—5	All staminate flowers removed	39	44	0	0	12	27·3
3—8	Natural set	30	30	15	33·3	15	50·0
4—10	Staminate flowers removed from half tree	27	36	23	39·0	18	50·0
5—10	Staminate flowers removed from half tree	39	43	5	10·4	23	53·5
6—14	Natural set	41	54	31	36·4	48	88·8
8—12	All staminate flowers removed	41	57	0	0	52	72·0
1—10	Natural set	71	140	250	64·1	126	90·0

Very small undeveloped staminate flower buds not counted.

$1/8-12$ and $1/3-5$, from which all staminate flowers had been removed, gave a surprisingly high percentage fruit set, indicating that this transference can be of considerable importance.

From the work outlined in this section it may safely be concluded that insects are necessary for Tung pollination, and that bees are probably the most important insects in this country. It may also be concluded that there is normally a sufficiency of pollen, at least in mature trees, and that where individual trees bear a low proportion of staminate flowers this may be made up by pollen transference from other trees. The extent of pollen transference which has been indicated is likely to be important where seed of high-yielding trees is selected for stud purposes, especially if " male " type trees are adjacent.

6. General Discussion.

The Tung plantation studied at Bargo by reason of the varied origins of the stock may be considered representative of the trees generally present in New South Wales. Climatic conditions at Bargo are not entirely satisfactory for Tung, particularly in regard to rainfall conditions, and the average yields obtained are naturally lower than those to be expected in the more satisfactory North Coast districts. The trees are well cared for, however, and it is indicated that the crop may prove profitable as a secondary proposition in conjunction with sheep, provided only high-yielding trees are planted.

Whilst a marked degree of variation is shown in all groups of trees, particularly in regard to yield and proportion of staminate flowers, some groups are much more uniform than others. In the groups chiefly studied, that is, the Bundanoon and Pennant Hills blocks, the majority of the trees are of very low yield, and at most 10 per cent. of the trees are satisfactory. It would thus appear that the degree of improvement possible by selection as well as by improved management of the trees is likely to be considerable.

The improvement of Tung yields should be attempted by all available methods. The climatic and soil requirements necessary are well known, and future plantings should be made only in districts which fulfil these conditions. A rainfall of 40 to 50 inches, fairly uniformly distributed, with the summer and autumn seasons neither too wet

nor droughty, a soil of slightly acid nature but well drained, and freedom from severe late frosts, are desirable.

The cultural treatment of the trees must also be satisfactory. Growth of green manure crops when the trees are young is probably advantageous, but cultivation may possibly be replaced by sown pasture when the trees are mature, provided these pastures are carefully managed.

One of the most important points in Tung culture is the necessity for effective windbreaks. These should be planted on all exposed sides of the groves even if a considerable portion of the land has to be so utilised. There is little information concerning the value of fertilisers for Tung in Australia, and such information is urgently desired.

Pruning, as a method of shaping and controlling Tung trees, is undesirable.[7]   Since the flowers are borne on the wood growth of the previous season, any pruning apart from the removal of dead or broken branches must necessarily reduce the following crop. Moreover it has been found at Bargo that the soft wood of the Tung is extremely liable to rot after exposure by pruning operations, and that this rot may often extend right to the base of the tree. As a consequence pruned trees have been found more liable to wind damage, and they have generally made unsatisfactory growth.

Drought conditions during the summer appear to influence adversely the following season's flowering in regard to the time of flower-bud initiation and the number of flowers produced. If practicable, irrigation during exceptionally dry summers and autumns would seem desirable.

A problem which faces many growers of Tung at the present time is the replacement of the large number of worthless trees by better yielding stocks. Replacement by means of the planting of the seedlings is a slow process, and until the inheritance of yield factors in Tung have been studied in detail it is by no means a certain method. Another method is the planting of young budded stock, but the results so far obtained by this method are not entirely satisfactory. A third method which might be adopted is to work over the unsatisfactory trees to better material by budding or grafting. No information appears to be available on this method, but at best it is likely to be only a stop-gap method.

METHODS OF TUNG IMPROVEMENT.

It has been shown that budded stock retains the characters of the parent trees from which the budwood is taken. The planting of young budded stock would thus be an ideal method for the attainment of uniform and high average yielding Tung groves. Unfortunately the experience with budded stock has not proved satisfactory, and consequently the development of pure breeding and high yielding seed strains becomes necessary.

In the planting of seedling Tung stock, the use of any or all seed available, regardless of its source, such as has been done in the past, must be abandoned. Only rigidly selected seedlings from parents of known high-yielding ability should be used, and a complete survey of the Tung groves in New South Wales is desirable for the purpose of selecting the best trees for stud seed production.

The methods available for the attainment of improved seed lines are several. The selection of seed from bulk, on the basis of attractive appearance, large size, or any other characters, is not only worthless, but definitely dangerous. Low-yielding trees are likely to produce large attractive fruits, and thus this method could result in actual selection of the low-yielding types.

The selection of seed in the groves from trees of known high yield over a period of years and with other desirable characters, and with due regard to the environmental conditions, offers a great advance over bulk selection. This is now being carried out by a number of growers. At Bargo blocks are being raised from seed selected on this basis, and valuable information should be obtainable from these in the future. The method, however, has definite limitations, which have been determined by the study of the pollination habits of the trees. The highest yielding trees have often a relatively small proportion of staminate flowers, and it has been shown that in such cases, especially when inferior " male " type trees are adjacent, considerable interpollination between the trees may occur. Consequently, the elimination of the undesirable type is not ensured by the selection of open-pollinated seed from the best trees. The most desirable method of selection would include some control of the pollen parentage as well as of the seed parentage of the stock.

The important characters upon which selection should be based are primarily the yield factors. In view of the correlations which have been described, however, vigour

of growth habit and similar characters should not be neglected. The desirability of the universally favoured Cluster type has also been brought into doubt. It has been shown at Bargo that the single fruiting type, by reason of the large number of fruiting spurs produced, possesses yielding ability not inferior to the Cluster type, and the latter is inclined to produce undesirable small fruits. In improvement work, both types should be followed up by selection.

Of the yield factors, number of fruits per tree is probably most important. Fruit size, the proportion of oil-bearing kernel, and the oil content of the kernel, however, may appreciably affect the total yield of oil, and demand attention. Analyses have shown that equal numbers of fruits from different trees may differ in oil yield by as much as 300 per cent.

The desirable Tung tree might be described as possessing the following characters : good vitality and vigour, inclination to produce a shapely tree suited to the bearing of high yields, and resistance to wind damage. The " umbrella " and " low branching " types are inferior in these respects. The trees should be, alternatively, of the Cluster or Single-fruiting type, and should produce a reasonable but not excessive proportion of staminate flowers. Most important, yields should be heavy, and the fruit large, with a high proportion of kernel and a high oil yield.

In Tung groves devoted to the production of stud seed a method of selection giving some control of pollen parentage might be adopted as an improvement upon the easier open selection. By the culling of all but the desirable trees from whole and preferably isolated blocks, only desirable pollen would be available. In blocks all the trees of which are derived from a single parent tree, this would amount to a method of line breeding similar to the Macauley method now adopted with maize, cucurbits, and other monoecious cross-pollinated crops. In groves planted intentionally for seed production, the seed from different parent trees should be planted separately in blocks not smaller than eight to ten trees each way to allow this system to be applied independently to those lines which later prove best.

A more exact method, giving more rapid attainment of uniformity within the line, would be careful inbreeding by the complete isolation or caging of desirable trees and hand pollination. Since a single tree of high yield would

be able to supply seed for a considerable area, this method would be quite practicable, especially if used to provide foundation blocks for the Macauley system of line-breeding. In view of the loss of vigour which usually follows continued inbreeding in the case of normally cross-pollinated plants, line-breeding may be preferable to inbreeding for the production of seed for ordinary commercial groves.

The value and possible results likely to be achieved by controlled cross-pollination between desirable distinct types and varieties cannot at present be indicated, but may be considerable. The method might be expected to offer more reasonable chances of success after the attainment of a measure of uniformity in the various types by in-breeding or line-breeding. Interspecific hybridisation may also give results of value, but with a cross-pollinated crop of long period, such as Tung, many years must elapse before uniformity could be obtained in such hybrids. Most rapid results are promised by rigid selection, combined with a control of pollen parentage, and line-breeding, with a more strict inbreeding for the separation of desirable and undesirable types.

SUMMARY.

1. A study has been made of Tung trees cultivated at Bargo, New South Wales.

It is apparent that satisfactory average yields cannot be expected from this grove owing to the high percentage of inferior trees. Profitable yields are likely to be obtained by planting only good selected stock.

2. Marked variation has been observed in such characters as habit of growth, proportion of staminate flowers and number of pistillate flowers per cluster, yields and size of fruit and properties of kernel.

Correlation has been indicated between some of the above characters.

3. The occurrence of pollen in abundance, at least in mature trees, has been demonstrated.

Considerable transference of pollen between adjacent trees has been shown to occur and the importance of this transference has been indicated in relation to selection work.

Male type trees are not necessary to ensure pollination.

4. Methods for the improvement of Tung trees have been discussed.

Although the planting of budded stock may offer a method of improving present groves, a more satisfactory means would be the development of high-yielding seed strains.

A method of line-breeding combined with limited inbreeding is considered the most suitable method of approach to this objective.

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THE REDUCTION OF SOME AROMATIC NITRO-COMPOUNDS BY HYDROGEN AND RANEY-NICKEL AT ATMOSPHERIC TEMPERATURE AND PRESSURE.

By Adrien Albert, B.Sc., Ph.D.,

and Bruce Ritchie, B.Sc.

The reduction of aromatic nitro-compounds to the corresponding amines by hydrogen with nickel catalyst is usually carried out at elevated temperatures, and it does not appear to be generally known that the reaction may be effected at room temperature and atmospheric pressure by using the special nickel catalyst devised by Murray Raney.[1] The reduction of nitrophenylene-diacrylic esters, recently described by Ruggli,[2] would appear to be the only recorded attempt to use nickel in this way. However, the vigorous nature of the reduction of nitro compounds by hydrogen and Raney-nickel under pressures ranging from 3 to 100 atmospheres (at temperatures up to 100°C.) has been described by Stevinson,[3] Adkins,[4] and Winans,[5] and this would suggest that successful, even if slower, reductions could be effected (in the cold) *at atmospheric pressure*. Reduction under these milder conditions could increase the availability of the method by dispensing with the need for special apparatus.

In the present work particular attention has been paid to the possible use of Raney-nickel in the synthesis of classes of amines whose preparation by other reduction methods is short of being satisfactory. Such, for example, are readily oxidisable diamines and aminophenols, for the production of which the proposed method appeared very attractive, as it would permit of working-up with a minimum of handling and exposure. Such, too, are substances (e.g., *m*-aminoformanilide) which are readily hydrolysed by the usual acid or alkaline reducing agents,

or which decarboxylate with abnormal rapidity (e.g., the substituted 2 : 4-diaminobenzoic acids, especially 5 : 5'-diaminodiphenylamine-2-carboxylic acid).

The results, summarised in the table, show that satisfactory yields of pure material were readily obtained, so that the method comes into consideration for preparing these and other primary aromatic amines on the small scale. Moreover the hydrogen absorbed is sufficiently close to theoretical requirements as to suggest the use of this method in determining the number of aromatic nitro-groups present in a substance known not to contain other easily reducible systems (such as the ketonic group or ethylenic linkage). The probability of groups being reduced under various experimental conditions is discussed in the book entitled "Reactions of Hydrogen" by Homer Adkins.[4] Winans's statement[5] that Raney-nickel does not remove (unactivated) chlorine from the benzene ring is of interest in this connexion.

The nickel used in this work was purchased in the form of inactive, finely-divided nickel-aluminium alloy,[6] which was activated by removal of the aluminium with sodium hydroxide. After preparation in this way, the catalyst, being pyrophoric in air, was stored under alcohol and appeared to retain its full activity for several months. The traces of iron present as impurity in the original alloy may be expected to cause the destruction of material especially sensitive to it but proved unobjectionable in the present work.

Full details of the reductions are given in the experimental section but the significance of certain of the results obtained will be discussed here. That the reduction follows the normal course: $R\text{-}NO_2 \rightarrow R\text{-}NO \rightarrow R\text{-}NH(OH) \rightarrow R\text{-}NH_2$, is suggested by the good yield of benzaldoxime-N-phenyl ether obtained when the partial reduction of nitrobenzene was effected in the presence of benzaldehyde. This reaction (Equation I) has been used by Vavon[7] to prove the production of phenylhydroxylamine in the reduction of nitrobenzene using a *platinum* catalyst.
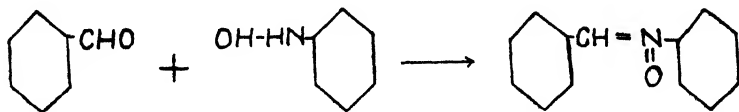
I.

One of the most interesting results obtained in this series was the successful reduction of two nitro-diphenylamine-2-carboxylic acids (5-nitro- and 5:5'-dinitro-) to the corresponding amino-acids. In earlier attempts to produce these acids, the commoner reducing agents had proved unsuccessful, causing decarboxylation to the corresponding aminodiphenylamines[8] (see Equation II).
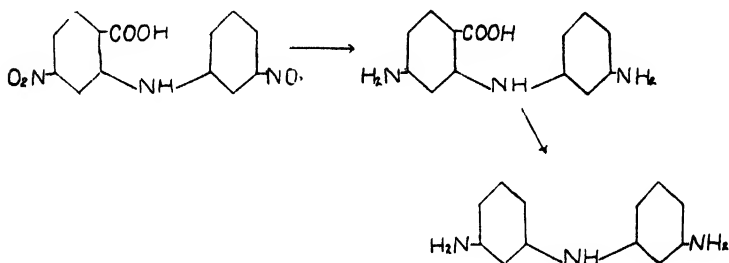
II.

This tendency of 2:4-diaminobenzoic acids to lose carbon dioxide was first pointed out by Seidel[9] and Ullmann[10] and discussed at length by Blanksma.[11] In comparing the properties of 2:4-diaminobenzoic acid and the two substituted acids prepared in the present work, it would appear that the tendency to decarboxylate increases in the presence of acids. The esters of these acids may be prepared, Bradbury and Linnell[12] readily obtaining the methyl ester of 5-aminodiphenylamine-2-carboxylic acid by the action of stannous chloride on the corresponding nitro-ester.

The reduction of 2:4-dinitrobenzaldehyde followed a remarkable course; since benzaldehyde was not affected under the experimental conditions, the reduction of the nitro-aldehyde to 2:4-diaminotoluene (Equation III) must be attributed to the activating influence of the substituent groups.

A preliminary investigation into the use of Raney-nickel and hydrogen in the acridine series was made. Acridone was unaffected, 2-nitroacridone gave 2-amino-acridone (m.p. 308°C. (corr.)), acridine was converted quantitatively to dihydroacridine and 1-nitroacridine gave

a mixture of 1-aminoacridine and (mainly) 1-aminodihydroacridine.
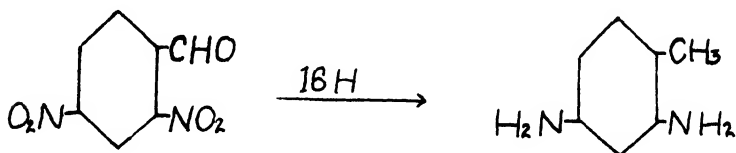
III.

EXPERIMENTAL.

Procedure.—The substance to be reduced was placed in a rubber-stoppered r.b. flask with 10 parts of alcohol and, except where otherwise indicated, one part of nickel (or its equivalent of alcoholic suspension). The air was exhausted from the flask, which was then connected to a graduated jar containing hydrogen (confined at the pressure of a few inches of water). The flask was mechanically shaken some 80 times a minute as in hydrogenation with platinum. At no time did the flask become more than 10° warmer than the surrounding air. Usually the absorption of hydrogen proceeded gently and regularly until some 70 per cent. had been taken up, after which reduction slackened but could be accelerated by immersing the flask for a few minutes in a basin of hot water. Finally, when the theoretical intake of hydrogen had been exceeded by some 5 per cent. absorption abruptly ceased. It was found necessary to pre-treat the rubber stopper by shaking it for ten hours with alcohol and catalyst. After surface-purification in this way the stopper may be used indefinitely without danger of spoiling the catalyst.

At the end of the reduction the flask was uncorked, warmed if the amine was not all in solution, and rapidly filtered from the nickel (which was at once transferred to alcohol). The filtrate was evaporated under reduced pressure in a current of nitrogen if needed. The catalyst was often fully active at the end of an experiment and could be used again. The use of water as a diluent in place of alcohol was unsuccessful; in fact reductions carried out in highly concentrated alcoholic solutions were observed to cease when a large proportion of water had accumulated, but could be completed by the addition of fresh alcohol.

Summary of Results. Reductions by Hydrogen and Raney-Nickel in Alcohol at Atmospheric Pressure.

Substance Reduced.	Amount Taken. g.	Time. (Hours.)	Hydrogen Absorbed. (Percentage of Theory.)	Yield. %	Substance Obtained.	M.pt. of Amine. °	M.pt. from Literature. °
m-Dinitrobenzene	1	2¼	102	88	m-phenylenediamine	63	63
2 : 6-Dinitrotoluene	1	2¼	109	90	2 : 6-diaminotoluene	103	105
Do. with 3 g. catalyst	25	16	110	91	2 : 6-diaminotoluene	103	105
2 : 4-Dinitrotoluene	1	2	102	96	2 : 4-diaminotoluene	97	99
2-Amino-4-nitrotoluene	1	1¼	101	93	2 : 4-diaminotoluene	95	90
2 : 4-Dinitrobenzaldehyde	1	2	—	75	2 : 4-diaminotoluene	97	99
3 : 5-Dinitrobenzoic acid	1	4	103	91	3 : 5-diaminobenzoic acid	226	236
o-Nitrophenol	1	½	108	98	o-aminophenol	165	170
m-Nitrophenol	1	½	106	81	m-aminophenol	121	121
3-Nitroformanilide	1	½	107	93	3-aminoformanilide	103	107
3 : 3' - Dinitro - N - formyl - diphenylamine	4	3	105	92	3 : 3' - diamino - N - formyl-diphenylamine	135	137
5 : 5'-Dinitrodiphenylamine-2-carboxylic acid	1	3	107	77	5 : 5'-diaminodiphenylamine-2-carboxylic acid	Dec.	New
5 - Nitrodiphenylamine - 2 - carboxylic acid	0·6	3	112	90	5 - aminodiphenylamine - 2 - carboxylic acid	140	New

Preparation of catalyst[a]: A solution of sodium hydroxide (75 g.) in distilled water (300 ml.) was placed in a 1-litre beaker cooled in ice and the alloy (75 g.) added over a period of two hours. The mixture was then heated at 110-115° for four hours with occasional stirring. More sodium hydroxide was then added (100 ml. of 20%) and heating continued until no more hydrogen was evolved (about 3 hours). After dilution to 750 ml., the supernatant liquid was decanted and the nickel washed six times by decantation. It was then washed at the pump until a neutral filtrate was given. Finally it was washed three times with 95% alcohol and stored under alcohol.

Detection of phenylhydroxylamine.—Nitrobenzene (2 g.), benzaldehyde (2 g.) and nickel (1 g.) were mixed with alcohol (20 ml.) and shaken with hydrogen until 708 ml. at 25° had been absorbed (time, 2 hours). On distilling off the alcohol and recrystallising the residue from light petroleum, copious white crystals of benzaldoxime-N-phenyl ether were obtained, having the recorded m.p. of 112°C.

m-**Dinitrobenzene** (1 g.) was completely reduced in 2½ hours, giving a 97% yield of crude *m*-phenylenediamine (m.p. 45°). After recrystallisation from benzene-*cyclo*hexane this became 88% and gave the correct m.p. of 63°.

2:6-**Dinitrotoluene** (1 g.) was reduced in 2 hours, giving a 97% yield of 2:6-diaminotoluene (m.p. 94°). After recrystallisation from water the melting point rose to 103° (recorded 105°). In another experiment, 25 g. of the dinitrotoluene and 3 g. of catalyst took 16 hours for reduction, resulting in a 91% yield of m.p. 103°.

2:4-**Dinitrotoluene** (1 g.) was reduced in 2 hours, giving a 96% yield of 2:4-diaminotoluene (m.p. 97°). After recrystallisation from benzene, this became 87% and gave the correct m.p. of 99°.

4-**Nitro-2-aminotoluene** (1 g.) was reduced in 1½ hours, giving a 93% yield of 2:4-diaminotoluene (m.p. 95°) which was readily purified as in the last example.

2:4-**Dinitrobenzaldehyde** (1 g.) reached equilibrium with hydrogen after 2 hours, taking up 780 ml. at 25-29°C. Diaminobenzaldehyde would require 748 ml. and diaminotoluene 998 ml. Hence the maximum possible amount of diaminotoluene produced would equal 80%. Actually the

acid-soluble material obtained was fairly pure diamino-
toluene (75%), m.p. 97°, and no other amines appeared
to be present. After recrystallisation it melted at 99°
(m.p. and mixed m.p.) and gave the following figures:

Found: C, 68·3; H, 8·6: $C_7H_{10}N_2$ requires C, 68·85;
H, 8·2%.

3:5-Dinitrobenzoic acid (1 g.) was reduced in 4 hours,
giving a 91% yield of diaminobenzoic acid (m.p. 226°).
After recrystallisation from water, the m.p. of 235°
(literature, 236°) was realised. An aqueous solution of
sodium 3:5-dinitrobenzoate absorbed no hydrogen even
on heating to 80° for 20 minutes.

o-**Nitrophenol** (1 g.) was reduced in 15 minutes, giving a
98% yield of *o*-aminophenol, m.p. 165°. After recrystal-
lisation from water the m.p. 169° (literature, 170°) was
reached. An aqueous solution of sodium *o*-nitrophenate
absorbed no hydrogen even on heating.

m-**Nitrophenol** (1 g.) was reduced in 45 minutes, giving
a 95% yield of *m*-aminophenol, m.p. 115°. After recrystal-
lisation from toluene, the recorded m.p. of 121° was
realised; yield 81%.

m-**Nitroformanilide** (1 g.) was reduced in 30 minutes,
giving a 93% yield of 3-aminoformanilide, m.p. 103°, not
depressed by admixture with an analysed specimen.

3:3′-Dinitro-N-formyldiphenylamine (4 g. + 3 g. catalyst)
was reduced in 3 hours, giving a 92% yield of 3:3′-
diamino-N-formyldiphenylamine, m.p. 135°. After recrys-
tallisation from alcohol, the correct m.p. of 137° was
obtained.

5:5′-Dinitrodiphenylamine-2-carboxylic acid (1 g.) was reduced
in three hours. About three-quarters of the material
obtained was soluble in ammonia and in dilute acids. It
formed minute white crystals, presumably the hitherto
unknown 3:3′-diaminodiphenylamine-2-carboxylic acid;
m.p. 71° with effervescence. After standing in the dry
state for three hours at room temperature it was found
completely decarboxylated, leaving a white solid insoluble
in ammonia. The m.p. was now 92·5° and no depression
of m.p. was given with an authentic specimen of 3:3′-
diaminodiphenylamine, m.p. 95°.

5-Nitrodiphenylamine-2-carboxylic acid (0·6 g.) was reduced
in 3 hours. The major part of the product was white,

soluble in ammonia, and was recrystallised from dilute alcohol, forming small white crystals of the hitherto unknown 5-aminodiphenylamine-2-carboxylic acid, m.p. 140°. Decarboxylation rapidly occurs on warming with dilute acid but the substance withstood a short boiling with water or dilute ammonia.

Found: N, 12·1; $C_{13}H_{11}O_2N_2$ requires N, 12·3%.

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SUBSTITUTED INDENES—Part I.

By V. M. TRIKOJUS, B.Sc., D.Phil., and D. E. WHITE, M.Sc., D.Phil.

During the course of investigations into the mobility of symmetrical triad systems by Ingold and collaborators, a study was made of the nature of the three carbon system in indene (I). Ingold and Piggott (*J.C.S.*, 1923,
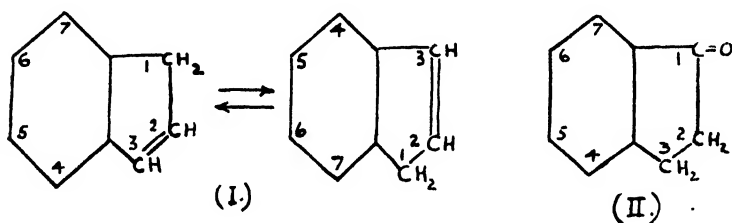
123, 1469) obtained the same substance, 5 (or 6)-methoxy indene, after pyrolysing the hydrochlorides of both 5- and 6-methoxy-1-hydrindamine. The indene nucleus thus satisfied the "symmetry test" of these authors, whilst furthermore two piperonylidene-methoxy-indenes were obtained on applying the "substitution test". Oxidative fission, however, yielded only the 5-methoxy derivative of the two possible homophthalic acids. Although it would be unusual in the indene series, the possibility that the two alkylidene derivatives were cis-trans isomers should not be excluded, and these results would then be consistent with an orientation of the substance as 5-methoxy-indene, the suppressed mobility thus implied being consequent upon the influence of the strongly directing methoxyl group.

In order to extend these studies, a number of substituted indenes have been prepared and are described in the present communication; 4:5-(or 6:7-) and 5:6-dimethoxy-, 5:6-methylenedioxy-, and 5(or 6)-methoxy

6(or 5)-ethoxy-indenes have all been obtained in good yield as colourless crystalline solids, by pyrolysis of the appropriate hydrindamine hydrochlorides (*cf.* Kipping and Hall, *J.C.S.*, 1900, **77**, 469), while we have repeated the preparation of 5(or 6)-methoxy-indene (from 5-methoxyhydrindamine hydrochloride). The action of bromine on 5(or 6)-methoxy-indene did not give the product described by Ingold and Piggott (*loc. cit.*), but a dibromo-compound m.p. 65-6°, which was easily decomposed by hydroxylic solvents. Bromination studies on the other indenes have also yielded some interesting results, and these, together with other experiments devised to test the nature of the double bond, will be reported in a subsequent communication.

Experimental.
5(or 6)-Methoxy Indene.

This was prepared from 5-methoxy-1-hydrindone (see Formula II) as outlined by Ingold and Piggott (*loc. cit.*, p. 1503), excepting that the amine hydrochloride was precipitated by the direct passage of dry hydrogen chloride into the ethereal solution of the base. The indene was obtained as a colourless oil with a strong, pleasant odour reminiscent of methyl salicylate. (This property was also characteristic of 5 : 6-dimethoxy indene, and, to a less degree, of the methoxy-ethoxy indene, whereas the other indenes described in this paper possessed odours more suggestive of the parent hydrocarbon.) It partly changes on keeping to a yellow solid, from which the unchanged indene may be separated by taking advantage of the latter's solubility in light petroleum.

Dibromide.—This was difficult to isolate owing to the ease with which it decomposed, and it was best prepared in anhydrous carbon bisulphide solution with pure dry bromine. Removal of the solvent in an evacuated desiccator yielded an oil, which rapidly solidified on treatment with light petroleum, from which it could be re-crystallised as small colourless aggregates, m.p. 65-66° with decomposition above 120° to a blue liquid (Found : Br = 51·6. Calc. for $C_{10}H_{10}OBr_2$: Br = 52·3%).

The dibromide is very soluble in most organic solvents and decomposes, on exposure to light, to a bluish-green

in colourless platelets, which decomposed at 254-255° (Found: N = 6·4; Cl = 16·5. Calc. for $C_{10}H_{12}ONCl$: N = 6·6; Cl = 16·6%).

5:6-methylenedioxyindene.—The hydrochloride was decomposed in small quantities (*ca*. 1 g) and the indene taken up in warm petroleum ether. The solvent was evaporated and the slightly yellow crystalline residue purified by distillation under reduced pressure. It formed colourless needles, m.p. 87-88° and could be preserved unchanged for long periods (Found: C = 74·95; H = 5·1. Calc. for $C_{10}H_9O_2$: C = 75·0; H = 5·0%).

5(or 6)-Methoxy-6(or 5)-Ethoxy-Indene.

5-Methoxy-6-ethoxy-1-hydrindone. — Phosphorus pentoxide (135 g.) was gradually added to β-(3-methoxy-4-ethoxy-phenyl)-propionic acid (55 g.; Slotta and Heller, *Ber.*, 1930, **63B**, 3029; Schlitter, *ibid.*, 1933, **66B**, 988) in benzene (150 c.c.) at the boiling point, and the mixture refluxed for 3-4 hours, cooled and decomposed with ice. The benzene layer was washed with alkali, dried and evaporated, the residual oil rapidly solidifying in contact with petroleum ether, yielding 27 g. of the hydrindone whilst 7 g. of the acid was recovered unchanged.. The *hydrindone* separated from benzene-petroleum ether in small, thick colourless prisms, m.p. 138-9° (Found: C = 69·9; H = 6·6. Calc. for $C_{12}H_{14}O_3$: C = 69·8; H = 6·8%). The *oxime* was readily obtained when the ketone was heated in alcoholic solution with hydroxylamine hydrochloride and sodium acetate. It formed pale yellow aggregates of needles from benzene, m.p. 188-9° (Found: C = 64·7; H = 6·6. Calc. for $C_{12}H_{16}O_3N$: C = 65·1; H = 6·8%).

5-Methoxy-6-ethoxy-1-hydrindamine hydrochloride.—The oxime (6·5 g.) was dissolved in the minimum volume of hot glacial acetic acid, water added to a faint turbidity, and reduction carried out by the gradual addition of sodium-amalgam (3%; 200 g.). The *hydrochloride* of the base was isolated as described above for analogous compounds. Yield 5 g. It separated from methyl alcohol in small colourless plates, which melted and decomposed at 268-270° (Found: Cl = 14·7. Calc. for $C_{12}H_{18}O_2NCl$: Cl = 14·6%).

5(or 6)-methoxy-6(or 5)-ethoxy-indene.—The amine hydrochloride (3 g.) was mixed with an equal volume of

powdered glass and heated at a bath temperature of $300°$ at 2.5 mm. The distillate was extracted with ether and the residue obtained on evaporation recrystallised from ether or aqueous methyl alcohol, from which it separated as rosettes of fine colourless needles, m.p. $65-66°$; yield 1.5 g. (Found: $C = 75.7$; $H = 7.6$. Calc. for $C_{12}H_{11}O_2$: $C = 75.8$; $H = 7.4\%$).

STRUCTURAL GEOLOGY OF THE MUDGEE-GUNNEDAH REGION.

By J. A. DULHUNTY, B.Sc.

(With Plate I and two text-figures.)

(Manuscript received, April 18, 1940. Read, May 1, 1940.)

CONTENTS.

NOTES ON THE MESOZOIC STRATIGRAPHY.

The area included in the Mudgee-Gunnedah region extends from Rylstone in the south to Gunnedah in the north, and Mendooran in the west to Murrurundi in the east. It is occupied mainly by Mesozoic strata, covered by Tertiary basalt in the central portion of the region. In the eastern and southern districts Kamilaroi beds outcrop strongly over considerable areas, and older Palæozoic rocks emerge from beneath the younger sediments in the south-western corner of the area and along the western side as small inliers.

The distribution and stratigraphical arrangement of the Mesozoic strata have been studied by several workers in the different districts which make up the area discussed in this paper. The stratigraphy of the different districts has been correlated[6] and the accompanying generalised geological map (Pl. I) illustrates the continuity of outcrop throughout the region. The geological boundaries in the north-western portion of this map are based on surveys carried out by Mr. E. J. Kenny in the Dunedoo, Coonabarabran and Gunnedah districts, in connection with the Geological Survey of New South Wales, and the eastern

margin of the Mesozoic strata between Murrurundi and Denman had been mapped by Dr. H. G. Raggatt before the area was examined by the present writer. For the detailed stratigraphy of the different districts, reference should be made to the original descriptions.[1-8]

The Kamilaroi and Triassic sediments, lying unconformably on the older Palæozoic rocks between Rylstone and Dunedoo, are shoreline deposits of lakes which extended north from the main areas of sedimentation in the Kamilaroi Basin. The northern shores of the lakes cannot be traced as they are covered by Jurassic beds. Their eastern margins appear to have been determined by the great zone of thrust faulting which extends along the eastern side of the Hunter Valley, crosses the main divide at Murrurundi, and passes away to the north-west through Quirindi and Gunnedah.

The Jurassic strata occupying the north and north-western portions of the Mudgee-Gunnedah region represent deposits which accumulated along the south-eastern shores of large freshwater lakes in which the sediments of the Great Artesian Basin were deposited. Actual shoreline facies occur in the vicinity of Cobborah, Dunedoo and Leadville, overlapping the Triassic and Kamilaroi beds at several places, where they rest unconformably on the basement rocks. Their southern shorelines seem to have passed to the east across the country now drained by the Goulburn River, and then turned sharply to the north, following to the north-west the line of thrust faulting, which at an earlier time had formed the shoreline of the Triassic and Kamilaroi lakes. It is evident that the south-eastern margin of the Jurassic lakes extended for a considerable distance over the north-western shorelines of Triassic sedimentation. Since the close of Jurassic time these areas have remained dry land, being elevated and eroded, and finally covered by the extrusion of basic lavas which built up the Liverpool Range in late Tertiary time.

STRUCTURAL GEOLOGY.

Structure of the Oxley Basin.

The name Oxley Basin is suggested for a structure which occurs within the Mudgee-Gunnedah region, extending south from Breeza and Tambar Springs to within fifteen miles of Rylstone, and west from Murrurundi to the vicinity of Coolah.

In the accompanying geological map (Pl. I) the Pottinger Beds, Garrawilla Series, and Gowen Beds, of Jurassic age, have been treated as one unit, separating the Triassic and Jurassic sandstones.   The narrow outcrop of this unit, which lies between the Triassic and Jurassic sandstone series, has been followed east from the vicinity of Dunedoo across the main divide and Goulburn River country to the Kingdon Ponds Valley near Scone, from which point it runs north to Murrurundi, where it is covered for a short distance by Tertiary basalt, but emerges again near Willow Tree and widens out, passing away first to the north-west then west across the southern Liverpool Plains to Coonabarabran.   From this locality the beds can be followed south, by the presence of large inliers, across the Binnaway district to Mendooran, and finally back to the Dunedoo district.   This constitutes a roughly circular belt, surrounding a large area of country occupied by Pilliga sandstone and Tertiary basalt, thus indicating a basin structure.   The direction of the dips determined at numerous places in the Triassic and Jurassic beds, and recorded on the accompanying geological map, confirms the presence of the basin-like structure.

The basin involves not only Jurassic and Triassic strata, but also the underlying Kamilaroi Coal Measures, and it is probable that the unconformable surface between the Kamilaroi and the older Palæozoic basement also conforms to the shape of the basin.

The structural margin of this basin (Pl. I) extends to the south far beyond the margin of the Jurassic beds, and also a considerable distance to the north of the marginal outcrops of the Pilliga sandstone along the northern side of the Liverpool Range.   This structure is both a basin of deposition and a tectonic structural unit.   The tectonic basin is somewhat elongated in a north and south direction, being 116 miles in length and 72 miles in width, and occupying an area of 6,200 square miles.   The area of the Pilliga sandstone in the central portion of the basin occupies only 2,800 square miles, while the area covered by the Pottinger Beds, Garrawilla Series, and Gowen Beds amounts to 3,600 square miles.

The depth of the basin at its centre is a matter of conjecture, as its central portion is completely covered by the basalts of the Liverpool Range, obscuring direct evidence. It is possible, however, to estimate its probable depth from indirect evidence, and thus obtain some idea of the shape

of the bottom of the basin, by studying the amount and rate of change of dips at the base of the Pilliga sandstone, along its outcrop, and also variations in the thickness of the different geological units. Such data would suggest that the base of the Jurassic strata is about 200 feet above sea level in the deepest portion of the basin, while the base of the Triassic sandstone would be about 300 feet below sea level, and the old Palæozoic rocks at the base of the Kamilaroi may be in the vicinity of 900 to 1,000 feet below sea level. The sections illustrated in text-figs. are based on the above data, in addition to direct evidence obtained from outcrops round the marginal areas of the basin.

Relation Between Structure and Stratigraphy.

Certain definite relationships exist between the structure of the Oxley Basin and the thickness and lithology of the strata which compose it. The following important features are illustrated in section A-B.

A submerged ridge of older Palæozoic rocks[6] is situated at the western side of the basin beneath the Coolah Valley. The Kamilaroi sediments thin out from the centre of the basin towards the ridge, pass over it and then tend to thicken slightly on the western side. The Triassic sandstone also thins out as it approaches the ridge, and continues to do so on the western side. The Jurassic shales representing the Pottinger Beds, Garrawilla Series, and Gowen Beds, thin to a marked degree as they pass over the ridge, and then develop rapidly on the western side, attaining a thickness greater than that which they possessed in the Oxley Basin. There is little evidence concerning the thickness of the Pilliga sandstone, as its upper surface has been removed by erosion. It is evident from field observations that the Tertiary erosion surface in this sandstone, preserved by the overlying basalt, rises in the vicinity of the submerged ridge. This could be the normal gradient of the old erosion surface, or may be due to late Tertiary warping following the extrusion of the basalts.

The foregoing evidence indicates that the old basement rocks formed a submerged ridge extending out into the Kamilaroi lakes. The Triassic sandstone thins out to the west and shows no local variations in thickness as it passes over the old ridge, which probably means that the basement at this point was not elevated immediately before, or during the deposition of the Triassic sandstone, but it must
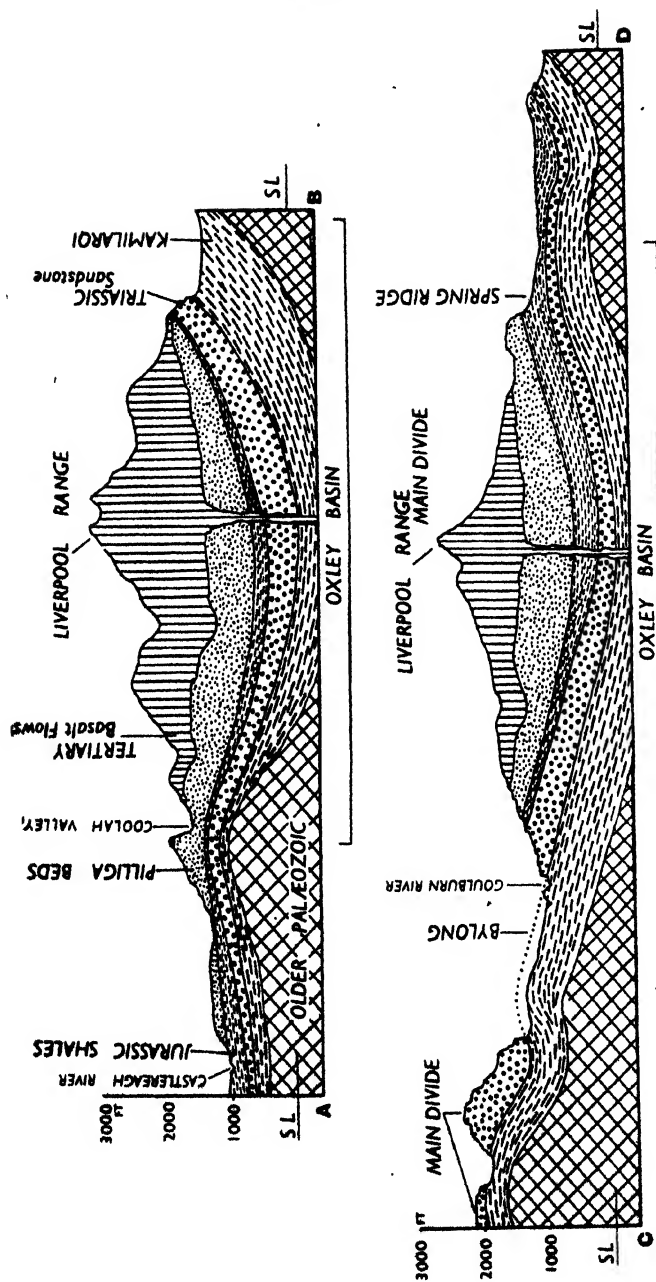
Fig. 1.—Sections A-B and C-D across the Mudgee-Gunnedah Region. Horizontal Scale : 8 miles to 1 inch.

have been elevated to a limited extent before the deposition of the Jurassic shales, as indicated by their development on both sides of the ridge.

At the eastern side of section A-B, it will be noted that the Kamilaroi beds do not thin out as they pass to the east, the Triassic are slightly reduced in thickness, and the Jurassic shales thin considerably, while the Tertiary erosion surface in the Pilliga sandstone rises gently. This suggests that there was practically no elevation of the eastern side of the Oxley Basin during Kamilaroi time, but some such upward movement must have commenced before or during the deposition of the Triassic beds, followed by more pronounced elevation in Jurassic time, which probably continued into the Tertiary era, warping the erosion surface of the Pilliga sandstone. As the basin is bounded on its eastern side by the zone of thrust faulting already referred to, the elevation of the strata evidently resulted from the thrust faulting. If this is so it may be concluded that the pressure responsible for the thrust faulting was active as early as late Kamilaroi time and continued into the Tertiary era.

In section C-D the following features are important : The Kamilaroi beds have their maximum development near the centre of the basin, and thin out both to the north and south, but they show no local variations in thickness as they pass over the small folds which determine the northern and southern margins of the Oxley Basin. The Triassic gradually decreases in thickness from south to north across the basin, and the Jurassic increases in thickness in that direction, both passing over the marginal folds without variations in thickness. There is evidence indicating slight elevation of the Tertiary erosion surface on the southern side of the basin, but not on its northern side. See section C-D.

These features suggest that the old basement rocks were warped into a gentle syncline before the deposition of the Kamilaroi sediments, and the folds which determine the northern and southern margins of the basin could not have come into being until after the deposition of the Jurassic shales, probably not till Tertiary time. Thus the elevation of the northern and southern sides of the basin appears to have been part of a process which commenced much later, and operated independently of that which caused the elevation of the eastern and western sides.

Associated Structures.

The Oxley Basin is surrounded by the following structures :

(a) The great zone of thrust faulting which runs along the eastern and north-eastern sides of the basin, and extends far beyond it in both directions.

(b) The northern margin of the tectonic limits of the Kamilaroi Basin, forming the south-eastern rim of the Oxley Basin between Rylstone and Muswellbrook.

(c) The elevated mass of Palæozoic basement rocks, running from Rylstone to Dunedoo, which represents a northern continuation of what must have been a mountainous coast-line extending along the western shores of the Kamilaroi lakes from as far south as Goulburn.

(d) The Great Artesian Basin lying to the north-west constitutes the most extensive adjoining structure. A small portion only of its south-eastern margin forms the north-western edge of the Oxley Basin.

(e) At the northern end of the Oxley Basin, a syncline, plunging to the north-west, forms a small indentation in its margin. Mr. E. J. Kenny first drew the author's attention to this structure. Its axis, coming in from the north-west, changes its direction of plunge about midway between Mullaley and Spring Ridge, at which point it enters the Oxley Basin and swings more to the south, its axis plunging gently in that direction, as illustrated by the dips recorded on the geological map (Pl. I). '

Origin of the Oxley Basin.

The origin of the basin is as complex as its structure, different portions having been formed at different geological periods, as the result of independent tectonic forces. The history of its origin, based on the evidence and conclusions contained in the preceding pages, is as follows :

Prior to Kamilaroi deposition, the Kamilaroi geosyncline commenced to develop and extended to the north-west, forming a low trough running through the Mudgee-Gunnedah region. Kamilaroi sediments were deposited in this trough, their western shorelines extending from Rylstone to Dunedoo. Towards the close of Kamilaroi time, upward movement associated with the Hunter Overthrust[9] amd Mooki Thrusts[10] commenced to elevate the strata between Muswellbrook and Gunnedah, thus reducing the width of the geosyncline and forming a narrow trough running north-west. In this trough freshwater

Triassic sediments were deposited, and towards the close of Triassic time further elevation occurred along its eastern side, and the submerged ridge of basement rock on its western side also underwent some elevation. The depression of the Great Artesian Basin probably commenced to form early in Triassic time and during the Jurassic period its lakes extended south-east into the northern portion of the Oxley Basin, previously occupied by Kamilaroi and Triassic waters.

The absence of Cretaceous sediments indicates that the Mudgee-Gunnedah region remained dry land during that period, while the Great Artesian Basin continued to sink. The folds which determined the structural margins of the Oxley Basin to the north and south originated after the deposition of the Jurassic sediments, as these beds were affected by the folding. The actual age of this cross-folding is uncertain, as it could have occurred during Cretaceous, Tertiary, or Pleistocene time, but it was probably associated with the major Tertiary uplifting of the Eastern Highlands of New South Wales, which produced a low tectonic trough running east and west from Newcastle towards Coolah.[5] At the southern end of the Oxley Basin this cross-folding produced the anticlinal structure which runs from Rylstone towards Muswellbrook, and at its northern end caused the syncline already mentioned to plunge in a southerly direction, southwards from a point about mid-way between Mullaley and Spring Ridge. This folding completed the structural building of the Oxley Basin.   .

The great mass of basalt up to 2,000 feet in thickness constituting the Liverpool Range is situated in the centre of the basin. At first sight this may suggest that the underlying strata have been depressed by the weight of the basalt. Such is not so, however, as the pre-basalt erosion surface in the Pilliga sandstone does not conform to the curvature of the beds in the basin, and the deeper strata are more strongly curved than those near the top, which means that the development of the basin commenced long before the late Tertiary basalt came into being. The fact that all the beds have their maximum thickness towards the centre of the basin, and thin out towards its margins confirms the conclusion that the basin was in existence during the deposition of the strata and long before the outpouring of the basalt.

SUB-SURFACE WATER SUPPLIES IN THE MESOZOIC STRATA.

The Pilliga sandstone provides the main aquifers of the Great Artesian Basin, and the underlying Jurassic sediments including the Pottinger Beds, Garrawilla Series, and Gowen Beds form an impervious substratum to the sandstone in the areas under discussion.

When the Jurassic strata associated with the intake beds of the Great Artesian Basin were found outcropping as far south as Merriwa, it was thought that they formed an additional area of intake beds, but this is not so, as water from the Oxley Basin cannot flow into the Great Artesian Basin.   On the accompanying geological map the elevation above sea level on the base of the Pilliga sandstone is marked at a number of points along its outcrop round the Oxley Basin.   These figures show that the base of the Pilliga sandstone, between Tambar Springs and Coolah, where it is continuous with the strata of the Great Artesian Basin, outcrops at an elevation of 1,400 to 1,500 feet. On the south-eastern side of the Oxley Basin its outcrop is only 770 feet above sea level at Merriwa.   This would seem to exclude any possibility of hydraulic communication between the two basins, and means that water accumulating in the Pilliga sandstone within the Oxley Basin would escape as surface water to the south-east before flowing into the Great Artesian Basin.   Evidence of such is to be found in permanent springs situated at the base of the Pilliga sandstone along the northern side of the valley of the Goulburn River and in its northern tributaries, from the vicinity of Turill on the Mudgee-Cassilis road to Bunnan on the Merriwa-Scone road.   These springs do not fluctuate with variations in annual rainfall, and their water, like that of the sub-artesian bores in the basin, is good stock water and only slightly mineralised, indicating that sufficient circulation is maintained in the Oxley Basin to prevent stagnation.

The Oxley Basin, which is a subsidiary structure on the margin of the Great Artesian Basin, may be termed a sub-artesian basin, as it contains supplies of sub-artesian water which have been tapped by bores round the margin of the Liverpool Range basalt.   The principal supplies of water are contained in the Pilliga sandstone.   The water rises a considerable distance in the bores which are situated some distance from the outcrop of the underlying impervious Jurassic shales, but the surface of the country does not fall

below the hydraulic grade at any point over the basin, due to the covering of basalt at its centre, and thus no artesian water is obtained. Had the Tertiary basalt not been extruded over the centre of the Basin, it is probable that there would have been small areas in which the hydraulic grade, taken from the base of the intake beds between Coolah and Tambar Springs to their base at Merriwa, would have been above the surface of the country.

In the southern and eastern sections of the Oxley Basin the Triassic sandstone is low in porosity compared with the Jurassic Pilliga Beds, and shows little evidence of providing aquifers, as the author is not aware of any true sub-artesian water supplies having been obtained from it. Several bores put down in this sandstone, well back from the outcrop of the Kamilaroi strata, have proved to be " dry holes ". In the north-western portion of the basin the Triassic becomes coarse and conglomeratic in its marginal facies, and it is probable that the porosity increases sufficiently to provide aquifers. These, however, would be limited in extent, as Mr. E. J. Kenny has shown that the Triassic thins rapidly to the north-west, and is eventually overlapped by the Pilliga sandstone. In the vicinity of Dunedoo and Gunnedah it extends beyond the margin of the Oxley Basin before the overlap occurs, but between these localities it is probable that the Triassic does not reach the margin of the basin, in some places.

ACKNOWLEDGMENTS.

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THE PREPARATION AND PROPERTIES OF SOME DIAZOAMINOAZO COMPOUNDS.

By F. P. DWYER, M.Sc.

The diazoaminoazo compounds R–N ꞊ N–NII - R–N = N–R have recently been the subject of some interest. Earl (THIS JOURNAL, 1930, *64*, 96) discovered that they occur normally in most diazoamino preparations unless special precautions are taken in regard to acidity during their preparation, and showed that benzenediazoaminoazobenzene is responsible for the red colour developed by diazoaminobenzene with alcoholic alkali. Further, the observation that the action of acids on diazoaminobenzene yielded considerable amounts of benzenediazoaminoazobenzene leads to the suggestion that the latter substance is an essential intermediate in the well known diazoamino/aminoazo transformation (Earl, *Ber.*, 1930, *63B*, 1666).

A method of removal of diazoaminoazo impurity from diazoamino compounds by adsorption on cadmium hydroxide has been described by the author (*J. Soc. Chem. Ind.*, 1937, *56*, 70 ; *J. Aust. Chem. Inst.*, 1938, *5*, 67) and 4-nitrobenzenediazoaminoazobenzene and 4-nitronaphthalenediazoaminoazobenzene have been recommended as sensitive spot reagents for the detection of cadmium (*J. Aust. Chem. Inst.*, 1936, *3*, 362 ; 1938, *5*, 37).

With the exception of the two nitrodiazoaminoazo compounds mentioned above, the parent substance benzenediazoaminoazobenzene is the only member of this class of substances described in the literature. For this reason, and in order to elucidate the mechanism of the cadmium spot test, a number of new compounds have been prepared and characterised.

The compounds are normally crystalline solids ranging in colour from orange yellow to deep red. They melt quite sharply, but like the diazoamino compounds explode if heated above their melting point. They are extremely sensitive to dilute acids, yielding instantly an aminoazo compound. The azo group apparently enhances the

acidity of the imino hydrogen, which is readily replace-able to yield highly coloured stable metallic salts. N-Methyl derivatives can be easily prepared by treatment with methyl iodide in alcoholic alkali. Characteristic reactions, which, however, fail with the N-methyl derivatives, are the formation of intensely coloured solutions in alcoholic alkali, and coloured lakes with cadmium and magnesium hydroxides.

EXPERIMENTAL.

N-Methylbenzenediazoaminoazobenzene.

Benzenediazoaminoazobenzene (3 g.) (Nietzki and Diesterweg, *Ber.*, 1888, *21*, 2143) in methanol (80 mls.) was refluxed with potassium hydroxide (0·56 g.) and methyl iodide (1·5 g.) until the initial intense red colour had changed to orange. Addition of water then pre-cipitated the compound, which was crystallised several times from dilute alcohol containing a trace of alkali. The orange yellow crystalline aggregates melted at 84–85°, and were quite soluble in acetone, benzene and chloroform. The substance gave no colour with alcoholic alkali, showed no salt-forming properties, and failed to adsorb on cadmium or magnesium hydroxides. It was decomposed instantly by dilute acids to an aminoazo compound.

Found: $N = 22 \cdot 17\%$; calculated for $C_{19}H_{17}N_5$, $N = 22 \cdot 22\%$.

2-Methylbenzenediazoaminoazobenzene.

p-Aminoazobenzene (5·9 g.) was ground up very finely with water (15 mls.) and concentrated hydrochloric acid (30 mls.) added gradually in small lots with thorough grinding between each addition. The suspension of the hydrochloride was then cooled to 4° C. and stirred mechanically whilst sodium nitrite (2·07 g.) dissolved in water (15 mls.) was added gradually over 10 minutes. The stirring was continued for a further 20 minutes and the dark red tetra-azo solution filtered rapidly from traces of unchanged p-aminoazobenzene. Urea (0·5 g.) was then added to destroy the excess nitrite and the cold solution neutralised to a faint turbidity with ice-cold saturated sodium carbonate solution. This solution was added immediately to an ice-cold solution of orthotoluidine (3·21 g.) in acetone (50 mls.), alcohol (50 mls.) and 3N sodium acetate solution (30 mls.). The substance, which

precipitated as a reddish oil crystallised on standing, and was crystallised several times from dilute alcohol in the presence of alkali. The orange yellow microcrystalline powder melted at 98°, and gave an intense red colour with alcoholic alkali.

Found : N $=22 \cdot 1 \%$; calculated for $C_{19}H_{17}N_5$, N $=22 \cdot 2 \%$.

2 - Methylbenzene - N - methyl - diazoaminoazobenzene prepared as before with methyl iodide and caustic potash gave orange yellow plates from aqueous alcohol, M.P. 88°.

Found : N $=21 \cdot 2 \%$; calculated for $C_{20}H_{19}N_5$, N $=21 \cdot 2 \%$.

3-Methylbenzenediazoaminoazobenzene.

Reaction between diazotised p-aminoazobenzene and metatoluidine gave a bright red precipitate, which consisted mostly of an aminoazo compound. The small amount of the required diazoaminoazo compound was separated by extraction with aqueous alcoholic caustic alkali, in which it was more soluble, and then precipitated by the addition of water. After several crystallisations from alcohol in the presence of a trace of alkali it gave reddish brown crystalline nodules, M.P. 96°.

Found : N $=22 \cdot 0 \%$; calculated for $C_{19}H_{17}N_5$, N $=22 \cdot 2 \%$.

3 - Methylbenzene - N - methyldiazoaminoazobenzene could not be isolated as it decomposed almost immediately on formation into an aminoazo compound.

4-Methylbenzenediazoaminoazobenzene.

This substance, prepared from diazotised p-aminoazo-benzene and paratoluidine, gave a brownish yellow micro-crystalline powder from alcohol, M.P. 158°.

Found : N $=22 \cdot 2 \%$; calculated for $C_{19}H_{17}N_5$. N $=22 \cdot 2 \%$.

4 - Methylbenzene - N - methyldiazoaminoazobenzene gave orange yellow aggregates from dilute alcohol, and melted at 121°.

Found : N $= 21 \cdot 1 \%$; calculated for $C_{20}H_{19}N_5$, N $=21 \cdot 2 \%$.

2-Nitrobenzenediazoaminoazobenzene.

The reaction between diazotised p-aminoazobenzene and orthonitraniline was found to take place only very slowly.

The substance was therefore made in the reverse manner from diazotised orthonitraniline and p-aminoazobenzene in alcoholic solution in the presence of sodium acetate. The voluminous orange yellow precipitate was crystallised from acetone in the presence of ammonia, and gave thin orange red rods and leaflets, M.P. 171–172°. The substance was apparently dimorphous since by crystallisation from aqueous acetone in the presence of ammonia a mass of fine woolly needles is first deposited, and then rapidly transformed into the leaflets and rods. This form may be isolated by shaking with warm acetone or hot benzene, in which it is the least soluble. The woolly needles melted at 171–172°, and did not depress the melting point of the other form.

Found :   N = 24·0% ;   calculated   for $C_{18}H_{14}O_2N_6$, N = 24·2%.

2 - Nitrobenzene - N - methyldiazoaminoazobenzene crystallised from boiling alcohol in the presence of a trace of alkali gave long orange yellow felted needles, easily soluble in benzene and chloroform, M.P. 132–133°.

Found :   N = 23·1% ;   calculated   for $C_{19}H_{16}O_2N_6$, N = 23·3%.

3-Nitrobenzenediazoaminoazobenzene.

This substance, prepared from diazotised metanitraniline and p-aminoazobenzene as before, gave bright red plates and prisms from acetone in the presence of ammonia, M.P. 185–186°. It was moderately soluble in benzene and chloroform.

Found :   N = 24·3% ;   calculated   for $C_{18}H_{14}O_2N_6$, N = 24·2%.

3 - Nitrobenzene - N - methyldiazoaminoazobenzene gave orange yellow matted needles from alcoholic alkali. The compound melted at 146°, was sparingly soluble in cold alcohol, but easily soluble in benzene and chloroform.

Found :   N = 23·0% ;   calculated   for $C_{19}H_{16}O_2N_6$, N = 23·3%.

4-Nitrobenzenediazoaminoazobenzene.

This substance has been recommended as a spot reagent for cadmium under the name " Cadion " (Dwyer, loc. cit.). The orange felted needles melted at 197°.

Found :   N = 24·2% ;   calculated   for $C_{18}H_{14}O_2N_6$, N = 24·2%.

4 - Nitrobenzene - N - methyldiazoaminoazobenzene gave orange yellow needles from aqueous acetone. The substance melted at 185–186°, and was sparingly soluble in alcohol, but easily soluble in benzene and chloroform.

Found : N $= 23 \cdot 1 \%$; calculated for $C_{19}H_{16}O_2N_6$, N $= 23 \cdot 3 \%$.

4-Nitronaphthalenediazoaminoazobenzene.

This substance prepared from diazotised 4-nitro-naphthylamine and p-aminoazobenzene has been recommended as the most sensitive reagent for cadmium under the name " Cadion 2B " (Dwyer, *loc. cit.*). It gave dark violet needles, M.P. 135°, from aqueous acetone. The substance could not be obtained in a pure state.

Found : N $= 19 \cdot 8 \%$; calculated for $C_{22}H_{16}O_2N_6$, N $= 21 \cdot 1 \%$.

4 - Nitronaphthalene - N - methyldiazoaminoazobenzene prepared from the above compound in the usual manner gave bright red curved needles, M.P. 195° (decomp.), from acetone. The substance was sparingly soluble in alcohol, but easily soluble in chloroform.

Found : N $= 20 \cdot 1 \%$; calculated for $C_{23}H_{18}O_2N_6$, N $= 20 \cdot 4 \%$.

Benzenediazoaminobenzene-4-azo-4'-nitrobenzene.

This substance, prepared from diazotised 4-nitro-4'-aminoazobenzene (Nolting, Binder, *Ber.*, **20**, 3015) and aniline, gave small red matted needles, M.P. 191° (decomp.), from acetone. The compound was sparingly soluble in most solvents.

Found : N $= 24 \cdot 3 \%$; calculated for $C_{18}H_{14}O_2N_6$, N $= 24 \cdot 3 \%$.

Benzene - N - methyldiazoaminobenzene - 4 - azo - 4' - nitrobenzene crystallised from alcohol in bright red needles, M.P. 191–192°. The substance was only slightly soluble in alcohol and acetone, but more soluble in benzene and chloroform.

Found : N $= 23 \cdot 5 \%$; calculated for $C_{19}H_{16}O_2N_6$, N $= 23 \cdot 3 \%$.

Preparation of the Cadmium and Magnesium Hydroxide Lakes.

These were prepared by the addition of a $0 \cdot 1 \%$ solution of the diazoaminoazo compound in alcohol containing a trace of alkali, to a neutral solution of the metal in the form

of nitrate or chloride, followed by an excess of caustic alkali. The colours of the various lakes are summarised in Table 1. The lakes were quite insoluble in water or alcohol, and were decomposed by traces of acid. The composition of the lakes is indefinite ; but they always contain an alkali metal. They are not simple adsorption compounds of the dyestuff on the metallic hydroxide, since they do not form unless there is an excess of caustic alkali above that necessary to precipitate the hydroxide. For this reason it is thought that it is the alkali metal salt of the diazoaminoazo compound that is adsorbed. The formation of the magnesium hydroxide lakes can be inhibited by the presence of sufficient sodium tartrate, provided that the solution is kept cold. The formation of the characteristic cadmium hydroxide lake is prevented by the addition of potassium cyanide. In this way it is possible to detect one metal in the presence of the other. The N-methyl derivatives yield no lakes with either cadmium or magnesium hydroxides.

TABLE 1.

Compound.	Colour with Alcoholic Alkali.	Magnesium Hydroxide Lake.	Cadmium Hydroxide Lake.
Bdaab ..	Red.	Magenta.	Salmon-pink.
2–CH$_3$–	Red.	Purplish-blue.	Brick-red.
3 CH$_3$– ,, ..	Red.	Purplish-blue.	Red.
4–CH$_3$– ,. ..	Red.	Purplish-blue.	Red.
2–NO$_2$– ,, ..	Reddish-purple.	Indigo-blue.	Orange-red.
3–NO$_2$– ,, ..	Purplish-red.	Magenta.	Orange-red.
4–NO$_2$– ,, ..	Purplish-violet.	Cornflower-blue.	Red-pink.
" Cadion 2B " ,.	Dark-blue.	Blue.	Scarlet.

Bdaab = Benzenediazoaminoazobenzene.

DISCUSSION.

In a previous paper (Dwyer, *J. Aust. Chem. Inst.*, 1938, 5, 149) it has been shown that the formation of coloured

magnesium hydroxide lakes with nitrodiazoamino compounds is always associated with the property of the dyestuff in yielding intensely coloured alcoholic alkaline solutions. This has been correlated with the migration of the imino hydrogen to the nitro group, and the resulting ortho or para quinoid structure is then responsible for the colour.

$$NO_2.C_6H_4.N = N-NH.C_6H_5 \rightarrow HO.O.N - C_6H_4 - N-N = N.C_6H_5$$

Such a tautomeric change is impossible with the meta nitro compounds, which show no marked colour change with alcoholic alkali, or with magnesium hydroxide.

In the nitrodiazoaminoazo compounds described in this paper a similar migration of the hydrogen to the nitro group is possible where the nitro group occupies an ortho or para position and might be offered as an explanation for the lakes with these compounds.

$$NO_2C_6H_4.N = N-NH.C_6H_4.N = N.C_6H_5 \longrightarrow$$
$$HO.O.N - C_6H_4 - N-N - N.C_6H_4.N - N.C_6H_5$$
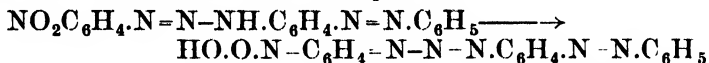
The explanation, however, obviously fails with the unsubstituted diazoaminoazo compounds, or those with a meta nitro group or with methyl groups, and focuses attention on the azo group. In this regard, it will be observed that the colours of all of the cadmium hydroxide lakes are similar, and if such colour identity is associated with an identical chromophore, the azo group is indicated. The evidence also shows that the formation of the lakes is associated with the property of forming intensely coloured alcoholic alkaline solutions—a reaction apparently due to salt formation. The N-methyl derivatives show no evidence of lake formation, give no colour with alcoholic alkali, and have no salt-forming properties.

It is thus clear that in the formation of the cadmium and magnesium hydroxide lakes, and of the coloured alcoholic alkaline solutions both the imino hydrogen and the azo group are implicated. The suggestion is made that the hydrogen may migrate from the triazene group to the azo group with the formation of a para quinoid structure.

$$C_6H_5.N = N-NH.C_6H_4.N = N.C_6H_5 \longrightarrow$$
$$C_6H_5.N = N-N = C_6H_4 = N-NH.C_6H_5$$
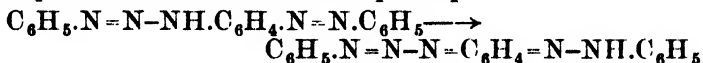
In alkaline solution an equilibrium probably exists between the alkali metal salts of the two forms, with the salt of the deeply coloured quinoid form predominating. In the presence of cadmium or magnesium hydroxides the alkali metal salt of the quinoid form is adsorbed with the formation of a coloured lake.

With the 2- and 4-nitro compounds the alternative migration of the hydrogen to the nitro group may occur, and this form is probably associated with certain of the deep blue magnesium hydroxide lakes. The iso-nitro form, however, is not implicated in any of the cadmium hydroxide lakes, since it has been shown in many previous papers (*loc. cit.*) that nitrodiazoamino compounds do not yield lakes with cadmium hydroxide. This is the basis of the method of purification of diazoamino compounds with cadmium hydroxide.

' ollowing the theory first put forward by Werner (*Ann.*, *1*, 669), and proved experimentally by Main-Smith and Morgan (*J. Chem. Soc.*, 1921, *119*, 704 ; 1922, *121*, 160), that mordant lakes are in reality chelate compounds, it is suggested that loose coordination complexes of type I occur probably at least on the surface of the cadmium and magnesium hydroxide lakes.

$$
\begin{array}{c}
\text{Na} \\
|
\end{array}
$$

$$C_6H_5.N = N - N = C_6H_4 = N - N.C_6H_5$$

$$M(OH)_2 \quad M(OH)_2$$

$$C_6H_5 - N - N = C_6H_4 = N - N = N.C_6H_5$$

$$\text{Na}$$

I

M = Mg or Cd
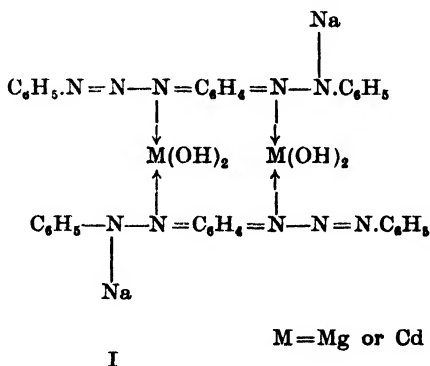
Department of Chemistry,
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COORDINATION COMPOUNDS WITH FURFURALD-OXIME AS A CHELATE GROUP.

PART I. ADDITION COMPOUNDS WITH METALLIC SALTS.

By A. BRYSON, M.Sc., B.App.Sc.,
and F. P. DWYER, M.Sc.

Since the oxygen of the furane ring has a lone electron pair, it should be capable of forming coordination compounds with metallic salts. In order to test this point a number of addition compounds with α and β furfuraldoxime and metallic salts have been prepared. The α (syn) oxime failed to yield any addition compounds with metallic salts, but rearranged under the influence of the metal to yield an addition compound of the β (anti) oxime. This reaction has been found to be a general one among syn aromatic oximes (Hieber and Leutert, *Ber.*, 1929, *62B*, 1839).

The compounds with the β oxime had the general formula $M.X_2.(C_5H_5O_2N)_{2 \text{ or } 4}$ which is the general constitution of a large number of oxime addition complexes examined by Hieber and Leutert (*ibid.*, 1927, *60B*, 2296), in which the metal oxime link is always through the nitrogen of the oxime.

Thus the furfuraldoxime addition compounds give no evidence of any coordination through the oxygen of the furane ring. In a subsequent paper, however, it will be shown that β furfuraldoxime can yield internal complex metallic salts in which this oxygen is involved.

EXPERIMENTAL.

The α and β furfuraldoxime were prepared by the method Brady (*J. Chem. Soc.*, *19*, 1959) and melted at 75-76° and 91-92° respectively. The addition compounds were prepared by the addition of an alcoholic solution of the oxime to an aqueous or alcoholic solution of the metallic salt. After standing a short time the precipitates were filtered off, recrystallised from alcohol or water, and

dried in the air. Unless otherwise stated, the β oxime was used in all of the preparations below.

I. Copper Salt Compounds.

(*a*) Cupric chloride dihydrate and the oxime, both in alcoholic solution, gave a brown precipitate immediately. Crystallised from methanol, in which it gave a green solution, brown needles of the bis compound were obtained. The compound was hydrolysed by water.

Found : Cu = 17·65%, Cl = 19·88% ; calculated for $Cu(C_5H_5O_2N)_2.Cl_2$, Cu = 17·73, Cl = 19·80%.

(*b*) Cuprous chloride was added to an alcoholic solution of the oxime and well shaken. The whole mass soon set solid, and was well washed with alcohol. Alternatively the compound could be prepared by the reduction of the cupric chloride compound above with sulphurous acid. The pure cuprous chloride compound was white, insoluble in alcohol and water, and rapidly transformed in the air into the brown cupric chloride compound. It was difficult to obtain pure.

Found : Cu = 20·3% ; calculated for $Cu(C_5H_5O_2N)_2.Cl$, Cu = 19·70%.

II. Silver Salt Compounds.

(*a*) Silver nitrate in aqueous solution and an alcoholic solution of the oxime gave a white crystalline precipitate, which was crystallised from hot water. The compound seemed to melt on heating, then exploded.

Found : Ag = 38·1% ; calculated for $Ag(C_5H_5O_2N)_2.NO_3$, Ag = 38·06%.

(*b*) Silver perchlorate in aqueous solution and the oxime gave a white crystalline precipitate, which was recrystallised from hot water. The compound was extremely soluble in alcohol.

Found : Ag = 24·9% ; calculated for $Ag(C_5H_5O_2N)_2.ClO_4$, Ag = 25·00%.

(*c*) Silver sulphate in saturated aqueous solution and an alcoholic solution of the oxime gave a white crystalline precipitate, which was recrystallised from hot water. The compound was insoluble in alcohol, and difficult to free from unreacted silver sulphate.

Found : Ag = 29·1% ; calculated for $Ag_2(C_5H_5O_2N)_4.SO_4$, Ag = 28·4%.

III. Nickel Chloride Compound.

Nickel chloride hexahydrate mixed with the oxime in alcoholic solution gave dense blue crystals, which were recrystallised from boiling alcohol. The compound was sparingly soluble in boiling benzene, but easily soluble in acetone.

Found : $Ni=10 \cdot 25\%$, $Cl=12 \cdot 43\%$;   calculated for $Ni(C_5H_5O_2N)_4.Cl_2$, $Ni=10 \cdot 16\%$, $Cl=12 \cdot 28\%$.

IV. Cobalt Chloride Compound.

Cobalt chloride hexahydrate and the oxime in alcoholic solution gave an orange brown crystalline precipitate.

Found : $Co=10 \cdot 31\%$, $Cl=12 \cdot 46\%$;   calculated for $Co(C_5H_5O_2N).Cl_2$, $Co=10 \cdot 20\%$, $Cl=12 \cdot 33\%$.

Reaction of α Furfuraldoxime with Metallic Salts.

Alcoholic solutions of α furfuraldoxime when added to alcoholic solutions of metallic salts yielded no precipitate nor gave any evidence of compound formation.   A mixture of the oxime and cupric chloride in methanol when allowed to stand for several hours deposited a brown crystalline precipitate.   After decomposition with water, the recovered oxime melted at 86°, and was thus almost pure β furfuraldoxime.

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A NEW SYNTHESIS OF NOR–NICOTYRINE, AND OF ITS OXYGEN ANALOGUE.

By FRANCIS LIONS, B.Sc., Ph.D.,
and ERNEST RITCHIE, M.Sc.

In Pictet's classical synthesis of nicotine (*cf.* Pictet and Crépieux, *Berichte*, 1895, *28*, 1904 ; 1898, *31*, 2018 ; Pictet, *ibid.*, 1900, *33*, 2355 ; Pictet and Rotschy, *ibid.*, 1904, *37*, 1225) N-(3'-pyridyl)-pyrrole (I), prepared by heating 3-amino pyridine with mucic acid, was caused to rearrange to nor-nicotyrine (II) by passing it through a red-hot tube. The nor-nicotyrine so obtained was converted by the action of methyl iodide on its potassium
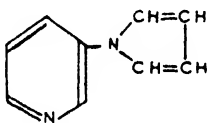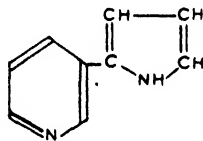
I   II

derivative to nicotyrine methiodide (III), from which nicotyrine (IV) was obtained by distillation with lime.
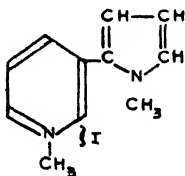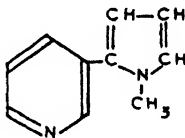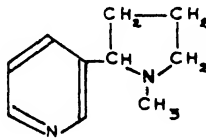
III   IV   V

Reduction of nicotyrine to nicotine was then effected by a rather lengthy series of reactions—a process much improved later by Späth and Kuffner (*Berichte*, 1935, *68*, 494), who carried out the reduction in one step by selective hydrogenation in presence of a palladium catalyst.

The Pictet nicotine synthesis involves violent and complicated reactions, which are inadequate to furnish

unequivocal proof of structures.   Indeed, following the demonstration by Wibaut and Dingemanse (*Rec. Trav. Chim.*, 1923, *42*, 1033) that thermal isomerisation of N-(2'-pyridyl) pyrrole leads to formation of both 2-(2'-pyridyl) pyrrole (VI) and 3-(2'-pyridyl) pyrrole (VII), it was shown by Wibaut and Gitsels (*Rec. Trav. Chim.*,
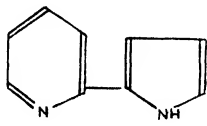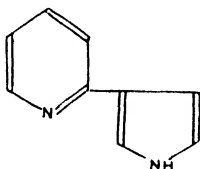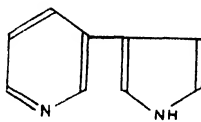
VI   VII   VIII

1938, *57*, 755), and by Späth and Kainrath (*Berichte*, 1938, *71*, 1276) that the passage of N-(3'-pyridyl) pyrrole (I) through a red-hot tube led to formation not only of nor-nicotyrine (II) but also of the isomeric 3-(3'-pyridyl)-pyrrole (VIII).

Because of the relative simplicity of Späth's (Späth and Kuffner, *loc. cit.* ; Späth and Kainrath, *loc. cit.*) improved Pictet nicotine synthesis, and the importance of nor-nicotyrine, it seemed of value to endeavour to prepare nor-nicotyrine by other methods, which would definitely confirm the constitution assigned to it.   One such preparation is described in this paper.

Benary (*Berichte*, 1911, *44*, 493) showed that when ethyl acetoacetate was treated with 10% ammonia and αβ-dichlorodiethyl ether, the latter reacted as chloro-acetaldehyde, and 2-methyl-3-carbethoxy-furan (IX) and the corresponding 2-methyl-3-carbethoxy-pyrrole (X) were formed :
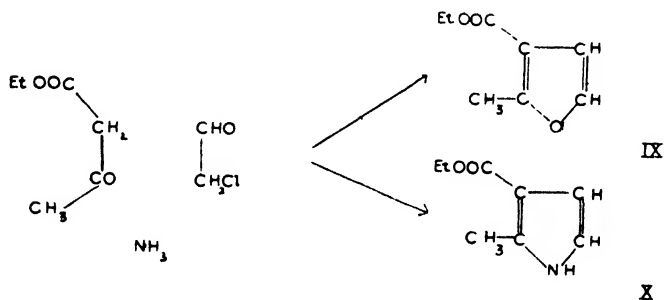
A similar reaction was applied to benzoylacetic ester by Fujita (*J. Pharm. Soc. Japan*, 1925, *519*, 4) and by Kondo and Suzuki (*ibid.*, 1927, *544*, 70), who showed that with this ester and αβ-dichlorodiethyl ether 10% ammonia yielded only 2-phenyl-3-carbethoxy-furan (XI) ; but that when 25% ammonia was used the corresponding 2-phenyl-3-carbethoxy-pyrrole (XII) was also formed.
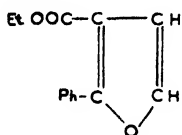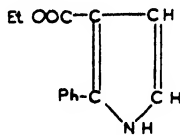
It appeared probable, therefore, that treatment of ethyl nicotinylacetate (XIII) with αβ-dichlorodiethyl ether and strong ammonia should yield 2-(3'-pyridyl)-3-carbethoxy-furan (XIV) and 2-(3'-pyridyl)-3-carbethoxy-pyrrole (XV) :
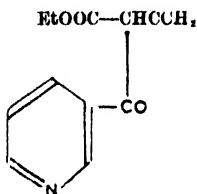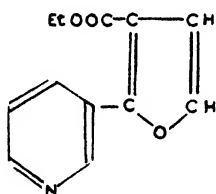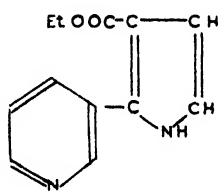
Hydrolysis of the pyrrole ester (XV), followed by decarboxylation, should yield nor-nicotyrine (II).

Experiment has shown that all these reactions can be realised. When ethyl nicotinylacetate, or its hydrochloride, was treated with αβ-dichlorodiethyl ether and 25% aqueous ammonia only the furan ester (XIV) was produced. However, if ammonia saturated at -5^{c} was used, the pyrrole ester XV was also formed, although only in small amount. Hydrolysis of this pyrrole ester to the corresponding acid (XVI) with alcoholic sodium hydroxide solution proved unexpectedly difficult, 30% of unchanged ester being recovered after 36 hours' refluxing with 10% alcoholic sodium hydroxide solution.

Heat treatment of a mixture of the pyrrole acid XVI with copper powder (" Naturkupfer C ") *in vacuo* led to smooth decarboxylation and formation of nor-nicotyrine (II), which was further characterised by its picrate.

The furan ester (XIV) underwent hydrolysis readily with hot alcoholic alkali, yielding the corresponding acid (XVII), which was also smoothly decarboxylated by heating with copper powder *in vacuo*. The resulting 2-(3'-pyridyl)-furan was a pleasant smelling oil, readily characterised by its crystalline picrate and methiodide.

EXPERIMENTAL.

2 - (3' - Pyridyl) - 3 - carbethoxy-furan (XIV) and 2-(3'-Pyridyl)-3-carbethoxy-pyrrole (XV).

Aqueous ammonia (100 ml.) was chilled in an ice-salt bath and saturated with ammonia at $-10°$ to $-15°$. The finely divided hydrochloride of ethyl nicotinyl acetate (Strong and McElvain, *J.A.C.S.*, 1933, *55*, 816 ; 20 g.) was added, and then to this vigorously stirred suspension $\alpha\beta$-dichlorodiethyl ether (20 g.) was added over a period of 15 minutes. Stirring and cooling were continued for two hours, after which the reaction mixture was allowed to stand overnight at room temperature. It was then extracted with chloroform, and the bases recovered from the combined filtered chloroform extracts with dilute hydrochloric acid. The acid extract was then quickly basified and the precipitated oil taken up, washed and dried in chloroform. After removal of the solvent the residual oil was fractionated *in vacuo*. An oil, A (5 g.), boiling at 147–153°/2 mms., and a dark gum, B, which boiled at 215–220°/2 mms. (approx.) were isolated. The gum, B, rapidly solidified, and after several recrystallisations from benzene yielded 2-(3'-pyridyl)-3-carbethoxy pyrrole (1·3 g.) in colourless needles melting at 118°. Treated with Ehrlich's reagent (an alcoholic solution of p-dimethylaminobenzoldehyde containing hydrochloric acid) in the cold a purple colour developed which deepened on standing or warming.

Found : $C=66·4$, $H=5·7$, $N=12·8\%$; calculated for $C_{12}H_{12}O_2N_2$: $C=66·7$, $H=5·6$, $N=13·0\%$.

The oil A, obtained above, was refractionated, and yielded a clear pale yellow oil (4 g.) boiling at 148–150°/1·5 mms. This was analysed.

Found : C $=66\cdot2$, H $=5\cdot0\%$; calculated for $C_{12}H_{11}O_3N$: C $=66\cdot4$, H $=5\cdot1\%$.

It was, thus, evidently *2-(3'-pyridyl)-3-carbethoxy-furan (XIV)*. Its *picrate* crystallised from alcohol in pale yellow needles melting at 153°.

Found : C $=48\cdot6$, H $=3\cdot4$, N $=12\cdot8\%$; calculated for $C_{18}H_{14}O_{10}N_4$: C $=48\cdot4$, H $=3\cdot2$, N $=12\cdot6\%$.

2 (3'-Pyridyl)-pyrrole-3-carboxylic acid (XVI).

A solution of the ester (XV ; $2\cdot5$ g.) in aqueous alcoholic sodium hydroxide solution (10 ml. of 10%) was refluxed for 36 hours, then diluted with water and freed from alcohol. After cooling, unchanged ester ($0\cdot8$ g.) was recovered with chloroform. To the aqueous solution was then carefully added just sufficient dilute hydrochloric acid to convert all sodium compounds to sodium chloride and it was evaporated to dryness. Hot water extracted the acid (XVI) from the red amorphous solid residue, and it separated again on cooling in small flattened pink needles ($0\cdot6$ g.) melting at 212–214° (with evolution of carbon dioxide).

Found : N $=14\cdot7\%$; calculated for $C_{10}H_8O_2N_2$: N $= 14\cdot9\%$.

2-(3'-Pyridyl) pyrrole (Nor-nicotyrine, II).

A mixture of the acid (XVI, $0\cdot6$ g.) with its own bulk of copper powder in a small distilling flask was heated at 230° *in vacuo* (pressure 2 mm.), Decarboxylation proceeded smoothly, and a clear colourless oil ($0\cdot3$ g.) distilled over and rapidly solidified to a mass of colourless needles. Recrystallised from a mixture of benzene and petroleum ether (in which solvent it exhibited a blue fluorescence) it was obtained in rosettes of colourless flattened needles melting at 98–99°.

Found : C $=74\cdot3$, H $=5\cdot7$, N $=19\cdot2\%$; calculated for $C_9H_8N_2$: C $=75\cdot0$, H $=5\cdot6$, N $=19\cdot4\%$.

Its *picrate* separated from alcohol in yellow leaflets melting at 203–204° (decomp.).

Found : N $=18\cdot5\%$; calculated for $C_{15}H_{11}O_7N_5$: N $=18\cdot8\%$.

Späth and Kainrath (*loc. cit.*) record the melting point of nor-nicotyrine as 95–97°, and that of its picrate as

200–202° (decomp.).   Wibaut and Gitsels (*loc. cit.*) record
the melting point of the base as 100–101°, and that of the
picrate as 202–203° (decomp.).

2-(3'-Pyridyl)-furan-3-carboxylic acid (XVII).

A solution of the ester (XIV ; 7·5 g.) in aqueous alcoholic
sodium hydroxide solution (25 ml. of 10%) was refluxed
for three hours, then cooled and treated with just sufficient
dilute hydrochloric acid to convert all the sodium com-
pounds present to sodium chloride.   After evaporating
to dryness the sodium chloride was dissolved out from the
powdered residue by stirring with the minimum necessary
quantity of water.   The residual acid was recrystallised
from alcohol, and thus obtained in small colourless needles
(6 g.) melting at 225°.

Found :   N=7·2% ;   calculated for $C_{10}H_7O_3N$:   N
7·4%.

2-(3'-Pyridyl)-furan.

The acid (XVII ; 6 g.) was mixed with copper powder
and decarboxylated exactly as described above for its
pyrrole analogue.   The oily distillate was taken up in
ether and freed from a little sublimed acid with sodium
hydroxide solution.   After drying and removal of the
ether it was redistilled, and a clear, colourless oil (4 g.)
was obtained, boiling at 127–128°/25 mm., exhibiting a
weak blue fluorescence, and possessing a pleasant flowery
odour somewhat resembling piperonal.

Found : C=74·1%, H=4·9% ; calculated for C_9H_7ON :
C=74·5, H=4·8%.

The *picrate*, crystallised from alcohol in long yellow
glistening needles melting at 152°.

Found :   N=20·3% ;   calculated   for $C_{15}H_{10}O_8N_4$:
N=20·5%.

The *methiodide* began to separate immediately when
2-(3'-pyridyl) furan was mixed with excess of methyl
iodide.   After some hours the excess methyl iodide was
removed, the residue washed with dry ether and recrystal-
lised from alcohol, from which it separated in small colour-
less needles melting at 221–222° (decomp.).

Found : C=41·3, H=3·6% ; calculated for $C_{10}H_{10}ONI$:
C=41·8, H=3·5%.

ACKNOWLEDGMENTS.

THE CONSTITUTION OF GMELINOL.

PART II.

By RITA H. HARRADENCE, M.Sc.,
and FRANCIS LIONS, B.Sc., Ph.D.

Receipt of most friendly and helpful suggestions, from Dr. H. Erdtman of Stockholm, and reprints from journals inaccessible to us, which we gratefully acknowledge, has led us to undertake a more careful purification of gmelinol and to reinvestigate its ultimate chemical composition, together with those of several of its derivatives which were described in Part I (THIS JOURNAL, 1937, LXXI, 391–405). Dr. Erdtman pointed out that frequently it has proved most difficult to obtain accurate analytical data for naturally occurring diarylbutanes unless a chromatographic adsorption analysis had been carried out prior to elementary analysis. In consequence, gmelinol was further purified by filtration of its solution in chloroform through a column of Brockmann's activated alumina, followed by recrystallisation from alcohol. The product was then submitted to analysis.

The results obtained in Sydney by Miss D. Little, B.Sc., were in close agreement with those obtained by Mr. Hall, of Oxford, and leave little doubt that gmelinol has the molecular formula $C_{22}H_{26}O_7$, rather than the formula $C_{21}H_{24}O_7$ previously suggested by Birch and Lions (Part I— *loc. cit.*). The molecular weight and methoxyl group determinations are also in good agreement with the formula $C_{22}H_{26}O_7$.

The analytical figures previously obtained by Birch and Lions (Part I—*loc. cit.*) for gmelinol phenylurethane, dibromo-gmelinol, and dibromo-iso-gmelinol agree very much better for the $C_{22}H_{26}O_7$ formula than for the $C_{21}H_{24}O_7$ formula. We have repeated the preparations of gmelinol phenylurethane and dinitro-gmelinol from pure gmelinol. Analysis of these derivatives carried out by Dr. G. Burger of Adelaide agree well with the $C_{22}H_{26}O_7$ formula for gmelinol.

A careful quantitative oxidation of gmelinol with potassium permanganate in acetone solution, according to the method used by Edrtman for pinoresinol dimethyl ether (*Sartryck ur Svenck Kemisk Tidskri*, 1938, 71) gave a 63% yield of veratric acid calculated on the assumption that two veratrole nuclei are present in the molecule— thus providing definite evidence of the presence of two such nuclei in the molecule.

This evidence for two veratrole nuclei, combined with the formula $C_{22}H_{26}O_7$, suggests the attractive possibility that gmelinol is a hydroxypinoresinol dimethyl ether. If this is so, six formulæ are possible for gmelinol, depending on whether pinoresinol is regarded as possessing formula I or II.

These six possibilities are formulated below :
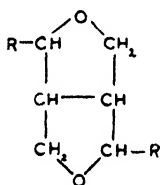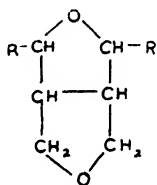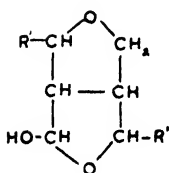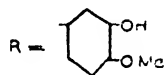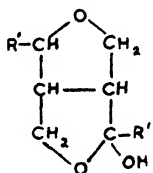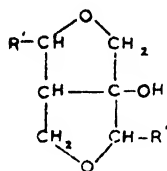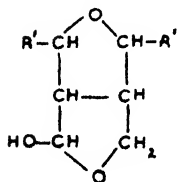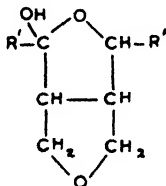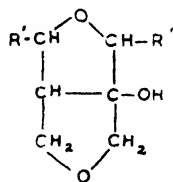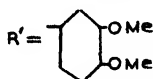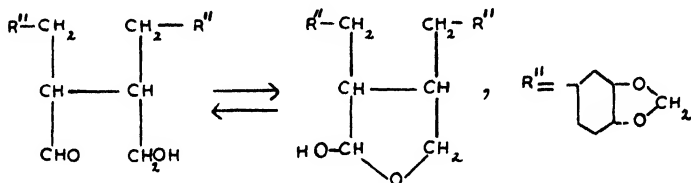
Substances corresponding to the formulæ III, IV, VI and VII would possess cyclic semi-acetal structures, and should be capable of existence in the open chain aldehydo-alcohol or keto-alcohol forms, as is cubebin, which is formulated as an equilibrium mixture of two isomeric forms :

$$R''-CH_2 \quad CH_2-R'' \qquad R''-CH_2 \quad CH_2-R''$$
$$CH \underline{\quad\quad} CH \rightleftharpoons CH \underline{\quad\quad} CH \, , \quad R''= \text{(structure)}$$
$$CHO \quad CH_2OH \qquad HO-CH \quad CH_2$$

Cubebin exhibits aldehyde reactions, giving a semi-carbazone and methyl cycloacetal, and being readily oxidised by mild oxidising agents to d-cubebinolide, the corresponding lactone. Nitric acid and bromine yield respectively dinitro and dibromo cubebinolide. It also loses water very readily with a variety of dehydrating agents, including halogen hydracids (especially hydriodic acid) in glacial acetic acid in the cold, oxalic acid, acetic anhydride, phosphorus pentoxide, phosphorus halides, acetyl chloride, etc., to give cubebin ether, which possesses a dihydrofuran ring. It can readily be reduced catalytically to dihydrocubebin (cf. Mameli, *Gazzetta*, 1907, *37*, 483 ; 1909, *39*, 494 ; 1912, *42*, 456, 551 ; 1921, *51*, 353 ; Ishiguro, *J. Pharm. Soc. Japan*, 1936, *56*, 444-52 ; Haworth and Kelly, *J.C.S.*, 1937, 387).

In contrast, gmelinol is not affected by mild oxidising agents, gives dinitro- and dibromo-gmelinol respectively on treatment with nitric acid and bromine, and gives no derivatives when treated with reagents for the carbonyl group—not even with hydroxylamine hydrochloride in pyridine solution, which usually reacts more readily than other carbonyl reagents with hindered keto groups. Moreover, gmelinol is not readily dehydrated. Isomerisation to isogmelinol occurs with the following dehydrating agents : iodine at 140° for 2·5 hours, phosphorus pentoxide in boiling xylene, sulphuric acid in acetic acid at room temperature for six days, anhydrous potassium hydrogen sulphate at 180° for thirty minutes, and concentrated hydrochloric acid in acetic acid for twenty-four hours. Gmelinol acetate can be distilled unchanged in high vacuum. Finally, gmelinol cannot be catalytically reduced,

so that the presence of an aldehyde group can be definitely
excluded. The presence of a keto group appears very
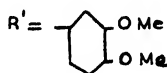unlikely also.

If gmelinol possessed either of the structures IV or VII,
it should be capable of existence in the open keto-alcohol
forms IX or X respectively,
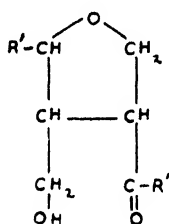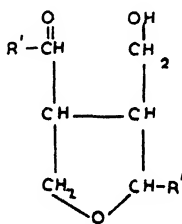
IX   X

in which the alcoholic group of IX would be primary in
nature. All the available evidence points strongly against
this possibility, and to the probability of the alcoholic
group being tertiary.

Up to the present it has not proved possible to isolate
any aldehydic or ketonic products during the oxidation
of gmelinol under mild conditions, except veratric aldehyde
(cf. Part I). Gmelinol can be recovered unchanged after
15 hours' heating with phthalic anhydride at 120–130° ;
and it is difficult to acetylate with acetic anhydride and
anhydrous sodium acetate. Smith reported acetylation
by this method, but we have not, so far, been able to
reproduce his successful experimental conditions. On
the other hand gmelinol acetate is readily obtained by
refluxing gmelinol with acetyl chloride for a short time.
The difficulty of formation of the phenyl urethane (Part I)
is also evidence for the tertiary nature of the hydroxyl
group. It would thus appear that, if gmelinol is a hydroxy-
pinoresinol dimethyl ether, only formulæ V and VIII
remain to be considered.

Attempts have been made, so far without success, to
remove the hydroxyl group from gmelinol and to compare
the resulting de-oxy gmelinol with pinoresinol dimethyl
ether. In the first series of experiments, replacement of
the hydroxyl group by a halogen atom, followed by
reduction, was attempted. Thionyl chloride alone reacted

with gmelinol to give an amorphous product melting at 190°. This was found to contain sulphur but no halogen. With thionyl chloride in pyridine solution two crystalline products melting at 202° and at 106° respectively were obtained. Each of these contains sulphur but no halogen. The products of interaction of gmelinol with phosphorus trichloride and with phosphorus pentachloride were resinous, and have not been thoroughly examined. Acetyl chloride, which frequently yields chloro compounds with tertiary alcohols, gave an acetate melting at 118° and distilling unchanged at 320°/3 mm., as noted above. Gmelinol could be recovered from it by alkaline hydrolysis.

In a second series of experiments attempts were made to remove the hydroxyl group by dehydration followed by hydrogenation of any olefine so obtainable. Fusion with anhydrous oxalic acid, or vacuum distillation with anhydrous potassium hydrogen sulphate, led to extensive decomposition. Other dehydrating agents, as pointed out above, gave isogmelinol together with varying amounts of tar. Since gmelinol and isogmelinol are isomeric and each contain one hydroxyl group (as shown by Zerewitinoff determinations) this reaction cannot be one of dehydration. It appears to be a stereochemical isomerisation of the type exhibited by pinoresinol dimethyl ether, sesamin, and asarinin, but no other isomers have been isolated.

Thus, up to the time of completion of the experiments herein described, no direct evidence in favour of either of the formulæ V or VIII has been obtained. However, Smith's observation that gmelinol vapour gives red and green colours with pinewood previously moistened with hydrochloric acid strongly suggests a furan skeleton.

EXPERIMENTAL.

Purification of Gmelinol.

Crude gmelinol (Part I) was freed from tarry material by filtration of a chloroform solution through a column of ordinary fine aluminium oxide, followed by recrystallisation from alcohol of the material recovered from the chloroform solution. The specimen for analysis was further purified by filtration of its chloroform solution through a column of Brockmann's activated alumina, followed by several crystallisations from alcohol.

Analysis of Purified Gmelinol.

Found (by Miss D. Little) :
    C$=65\cdot6$, $65\cdot7\%$; H$=6\cdot4$, $6\cdot4\%$.
Found (by Mr. Hall, Oxford) :
    C$=65\cdot94$; H$=6\cdot56\%$.
    Molecular weight$=411$.
    Methoxyl$=28\cdot8\%$.
Calculated for C$_{21}$H$_{24}$O$_7$:
    C$=65\cdot0\%$; H$=6\cdot2\%$; molecular weight$=388$;
        methoxyl$=31\cdot9\%$.
Calculated for C$_{22}$H$_{26}$O$_7$:
    C$=65\cdot7\%$; H$=6\cdot5\%$; molecular weight$=402$;
        methoxyl$=30\cdot8\%$.

Gmelinol, thus, is almost certainly C$_{22}$H$_{26}$O$_7$, and the
values obtained by Birch and Lions (Part I—*loc. cit.*)
for molecular weight (400) and for methoxyl ($30\cdot2\%$)
agree better for this formula.

Number of Free Hydroxyl Groups in Gmelinol.

A Zerewitinoff determination of active hydrogen was
carried out on gmelinol in xylene solution. A colourless
precipitate was formed immediately on mixing with methyl
magnesium iodide solution. Although the values obtained
were low (about 60% of theory for one hydroxyl group)
they indicate the presence of one hydroxyl group in the
molecule.
    Found : OH$=2\cdot6$, $2\cdot9$, $2\cdot6\%$; calculated for
C$_{22}$H$_{25}$O$_6$(OH) : OH$=4\cdot2\%$.

Analyses of Derivatives of Gmelinol.

  (a) *Dinitrogmelinol (from purified gmelinol).*
    Found (by Dr. Burger, Adelaide) :
        C$=52\cdot8$, H$=5\cdot2$, N$=5\cdot8\%$; calculated for
        C$_{22}$H$_{24}$O$_{11}$N$_2$: C$=53\cdot6$, H$=4\cdot9$, N$=5\cdot7\%$.
  (b) *Gmelinol Phenylurethane (from purified gmelinol).*
    Found (by Dr. Burger, Adelaide) :
        C$=66\cdot9$, H$=5\cdot9$, N$=2\cdot8\%$; calculated for
        C$_{29}$H$_{31}$O$_8$N : C$=66\cdot8$, H$=6\cdot0$, N$=2\cdot7\%$.
  (c) *Dibromo gmelinol.*
    Found (Birch and Lions, *loc. cit.*) :
        C$=47\cdot0$, H$=4\cdot2\%$; calculated for C$_{22}$H$_{24}$O$_7$Br$_2$:
        C$=47\cdot2$, H$=4\cdot3\%$.

(d) *Dibromoisogmelinol.*

　Found (Birch and Lions, *loc. cit.*) :
　　$C = 47 \cdot 0$, $H = 4 \cdot 2 \%$; calculated for $C_{22}H_{24}O_7Br_2$:
　　$C = 47 \cdot 2$, $H = 4 \cdot 3 \%$.

Oxidation of Gmelinol with Potassium Permanganate in Acetone Solution.

　Finely powdered potassium permanganate was added in one gram portions at hourly intervals to a frequently shaken solution of gmelinol (10 g.) in pure acetone (400 ml.). The oxidation was spread over several days and was complete after addition of twenty-eight grams of potassium permanganate.　After standing twenty-four hours it was filtered.. The manganese dioxide sludge was washed with ether and dried in the air.　The filtrate was decolourised with sulphur dioxide, filtered and distilled.　The residual unchanged gmelinol was negligible in amount.

　The manganese dioxide sludge was suspended in water (100 ml.) to which dilute sulphuric acid (100 ml. of 4N) was gradually added.　Much carbon dioxide was evolved during this acidification.　The manganese dioxide was then taken into solution by passing sulphur dioxide whilst keeping the solution cold.　The undissolved veratric acid was eventually collected, washed and dried (7 g.).　On sublimation in high vacuum this crude material gave $5 \cdot 7$ grams of almost pure veratric acid.　The theoretical yield from 10 grams of pure gmelinol, calculated on the presence of two veratrole nuclei, is $9 \cdot 1$ grams.　The percentage yield is therefore 63%.

Gmelinol Acetate.

　Gmelinol (5 g.) was refluxed with acetyl chloride (30 ml.) for one hour.　Most of the excess acetyl chloride was then distilled off and the residue treated with water.　The oil was induced to crystallise and after washing with alkali and water it was collected and recrystallised from alcohol, being thus obtained in colourless prisms melting at 118° (mixed melting point with gmelinol about 110°).　This ester can be distilled unchanged, and boils at $320^{\circ}/3$ mm.

　Found : $C = 64 \cdot 6$, $H = 6 \cdot 4 \%$; calculated for $C_{24}H_{28}O_8$: $C = 64 \cdot 8$, $H = 6 \cdot 3 \%$.

　Gmelinol can be recovered from this acetate by hydrolysis with alcoholic potash.

Action of Dehydrating Agents on Gmelinol.

(1) **Anhydrous oxalic acid.** Fusion of gmelinol with anhydrous oxalic acid at 180° caused extensive decomposition.

(2) **Iodine.** Gmelinol (1 g.) was heated at 140° with a trace of iodine for 2·5 hours. Recrystallisation from alcohol gave colourless plates melting at 135°. Repeated recrystallisation raised the melting point to 148°, and this showed no depression with an authentic specimen of *isogmelinol.* Isomerisation had therefore occurred; but it was shown not to occur on heating gmelinol alone at 140° for 2·5 hours.

(3) **Phosphorus pentoxide.** Gmelinol (2 g.) was refluxed with phosphorus pentoxide (5 g.) in dry xylene (20 cc.) for fifteen minutes. The phosphorus pentoxide turned black and a certain amount of tar was formed. The xylene solution, which possessed a red colour and a slight green fluorescence, was decanted, boiled with charcoal, filtered and cooled rapidly, when some tar separated. The solution was decanted from the tar and on scratching deposited crystals. Several crystallisations from ethyl acetate gave *isogmelinol,* melting at 148° and giving no melting point depression with an authentic specimen.

(4) **Sulphuric acid in acetic acid.** Gmelinol (1 g.) was dissolved in glacial acetic acid (10 cc.) and a few drops of concentrated sulphuric acid added. A slight violet colour developed, changing to green. The solution was allowed to stand six days, then poured into water and made alkaline. The product, on recrystallisation from alcohol proved to be *isogmelinol.*

(5) **10% Alcoholic hydrogen chloride.** When gmelinol was refluxed with 10% alcoholic hydrogen chloride a brown colour developed, and a brown resin was obtained on pouring into water.

(6) **Hydrochloric acid in acetic acid.** Gmelinol (1 g.) was dissolved in acetic acid (3 cc.) and concentrated hydrochloric acid (6 cc.) added. The solution was allowed to stand twenty-four hours, during which time a dark brown colour developed. The gum obtained on pouring into water solidified after treatment with alkali and scratching for some time. Recrystallisation from alcohol gave a small amount of *isogmelinol.*

(7) **Anhydrous potassium hydrogen sulphate.** Attempted vacuum distillation with anhydrous potassium sulphate caused extensive decomposition.

Gmelinol (1 g.) was intimately mixed with potassium hydrogen sulphate (2 g.) and heated at 180° for thirty minutes. Besides much tarry material a small amount of isogmelinol was isolated by recrystallisation from alcohol.

Preparation of Isogmelinol.

The method described in Part I (*loc. cit.*) for the preparation of isogmelinol, viz., refluxing with 20% aqueous formic acid for ten hours, with or without addition of alcohol, yields a mixture of gmelinol and isogmelinol from which pure isogmelinol can be isolated after several recrystallisations—eight usually being necessary. By refluxing for twenty-four hours the conversion is more complete, but a considerable amount of tar is formed and the product is difficult to purify.

A better method for the preparation of isogmelinol has been elaborated. It consists in adding a few drops of concentrated sulphuric acid to an acetic acid solution of gmelinol, and allowing the mixture to stand for six days. The isogmelinol is then isolated by dilution with water and basification. The product may be recrystallised from alcohol, ethyl acetate or xylene. It separates from the latter solvent in colourless prisms melting at 149°.

Found : C = 65·7, H = 6·5% ; calculated for $C_{22}H_{26}O_7$: C = 65·7, H = 6·5%.

The *rotation* of isogmelinol was determined in chloroform solution. A solution of isogmelinol (0·1 g.) in chloroform (10 ml.) in a 1 decimetre tube gives a rotation of + 0·30° at 15° with sodium light. This gives a specific rotation of $[a]_D = + 30°$.

The presence of a hydroxyl group in isogmelinol was shown by a Zerewitinoff active hydrogen determination. This was carried out in warm xylene solution, a colourless precipitate forming on mixing with the solution of Grignard reagent.

Found : OH = 3·7% ; calculated for $C_{22}H_{25}O_6$ (OH) : OH = 4·2%.

An attempt to prepare an *acetate* from isogmelinol with acetyl chloride gave a clear gummy product which could not be induced to crystallise.

Attempts to prepare a *phenyl urethane* proved abortive, isogmelinol being recovered unchanged.

Attempted Replacement of the Hydroxyl Group in Gmelinol with Halogen.

(1) **Thionyl chloride.** Gmelinol (5 g.) was refluxed with thionyl chloride (50 ml.) for one hour. Most of the thionyl chloride was removed and the residue poured into water. The gum which first precipitated solidified on rubbing. It was filtered off and washed with alkali and water. It came out from alcohol as a pale yellow amorphous solid, melting at about 189-190° and containing sulphur but no halogen.

This behaviour is unusual for tertiary alcohols, which generally give chloro compounds with thionyl chloride, whilst primary and secondary alcohols give sulphurous esters. The above compound, however, is not of the nature of an ester. On heating with sodium hydroxide solution it first becomes oily and then finally dissolves. However, on acidification an amorphous compound melting about 190° and containing sulphur is obtained. This is probably identical with the original material, which has not been analysed.

The alcoholic filtrate from this amorphous material deposited crystals on standing overnight. Recrystallised from alcohol these were obtained as pearly plates melting at 160°, but there was insufficient material for a sodium fusion and chemical examination or analysis.

(2) **Thionyl chloride in pyridine.** Gmelinol (10 g.) was dissolved in pyridine (10 g.) and an equimolecular quantity of thionyl chloride (2 cc.) added gradually. Reaction occurred with evolution of heat. The resultant mixture was heated on the water bath for ten minutes, then poured into water and acidified. The precipitate was filtered off and washed. After drying it was taken up in alcohol, charcoaled, and filtered. Small crystals gradually separated from the brown solution on standing overnight. These were filtered off and recrystallised several times from alcohol, in which they were sparingly soluble. Almost colourless prisms melting at 202° were

thus obtained. The substance contains sulphur but no halogen. It is stable to boiling concentrated hydrochloric acid.

The alcoholic filtrate from these crystals was allowed to stand for some days, when another substance crystallised out in rosettes of small needles, melting at about 100° in the crude condition. After recrystallisation from alcohol soft colourless needles melting indefinitely were obtained. These softened at about 100°, fused to a transparent glass on the sides of the tube at 106°, but did not become mobile* and subside till about 150°. At higher temperatures darkening in colour occurred. Several recrystallisations from alcohol did not improve the melting point. The substance separates from alcohol as a mixture of gum and crystals, the gum gradually changing to the crystalline form. It is soluble in hot methyl and ethyl alcohols, ethyl acetate, benzene and dioxan, sparingly soluble in ligroin and insoluble in petroleum ether and water. It also contains sulphur but no halogen.

Found: C = 60·6, 60·1%; H = 6·1, 6·0% : $C_{22}H_{26}O_5S_2$ demands C = 60·8, H = 6·0%.

A sulphur estimation has not been carried out, nor has the molecular weight been determined.

A solution of the substance (0·4 g.) in glacial acetic acid (10 ml.) gave an angle of rotation a = + 1·23 in a 5 cm. tube at 19·5°, which corresponds to a specific rotation of $[a]_D$ = + 61·5°. The rotation of gmelinol has therefore been reduced by about half.

(3) **Phosphorus trichloride.** Gmelinol (1 g.) was refluxed with phosphorus trichloride for twenty minutes. The solution was decanted from a small amount of tar and poured into water. The gum which precipitated solidified. It could not be crystallised, separating as a clear gum from all solvents.

(4) **Phosphorus pentachloride.** Gmelinol (1 g.) suspended in carbon tetrachloride was added to phosphorus pentachloride (2·5 g.) in carbon tetrachloride. The mixture was refluxed until complete solution occurred. A red colour developed and hydrogen chloride was evolved. The mixture was poured into water, the carbon tetrachloride layer washed with alkali and water and dried. Removal of the solvent left a resin which could not be crystallised.

The action of phosphorus pentachloride on gmelinol in benzene in the presence of pyridine gave rise to tarry products which were not examined.

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CORRIGENDA.

Page 136, for (c), (d) and (e) *read* (d), (e) and (f);
'ine 18, for (c) *read* (d).

Page 138, line 3, for (c) *read* (d).

THE SIGNIFICANCE OF LARGE BOND ANGLE DISTORTIONS IN RELATION TO THE STEREOCHEMISTRY AND MAGNETIC PROPERTIES OF QUADRICOVALENT METALS.

By D. P. MELLOR, M.Sc.

BOND ANGLE DEFORMATION IN RELATIVELY SIMPLE MOLECULES.

The existence of bond angles differing considerably from the tetrahedral value of 109° 27' has long been known among alicyclic compounds and has formed the subject of a special theory generally referred to as Baeyer's[1] strain theory. Baeyer assumed that the normal tetrahedral angle of carbon bonds could be markedly changed to values above or below the theoretical value. Any deviation from the tetrahedral angle was supposed to introduce strain, with consequent decrease in the stability of a molecule. Baeyer's theory, which referred specifically to distortion of carbon bond angles, is still valid for rings smaller than cyclohexane in which angles less than 109° 27' are found, but it is becoming increasingly clear that this theory of bond deformability can be extended to other atoms and to instances of bond angle deformation brought about by means other than ring formation.

Recent electron diffraction, X-ray, and other studies have thrown light on the question of bond deformation. It has been found, for example, that in cyclopropane,[2] while the distortion of 49° produces no effect on the length of the C–C bond, which is that of a single bond, it does diminish the stability of the molecule, the heat of formation of which is some 23 kcal/mole less than that calculated from the bond energies.[3] Electron diffraction studies of ethylene oxide[4] lead to the following bond lengths : C–C$=1\cdot56$ A., C–O$=1\cdot45$ A., which imply bond angles C $\diagdown$ O 58° and C $\diagdown$ C 64° respectively. Corresponding data for ethylene sulphide and ethylene

imide are not yet available, but large distortions from the 90° angles for S< and H–N<* bonds must also occur in these molecules. In the tetrahedral molecules of As_4 and P_4,[5] which have also been examined by electron diffraction, there occur bond angles of 60°, which represent a distortion of 30° from the value 90°, predicted theoretically and found experimentally, for other compounds of arsenic and phosphorus.

The recent analysis[6] of the structure of crystalline PdS also presents several points of interest in connection with the question of bond deformation. Normally, four bonds to S are tetrahedrally disposed, while four bonds to Pd^{II} are directed towards the corners of a square. Neither of these ideal configurations is realised in the crystal of PdS, but, instead, a compromise between the two ; thus the angles between the palladium sulphur bonds

Pd
(S⌒   ⌒S) vary from 77° to 100°, while some of the
S

Pd⌒ ⌒Pd bonds deviate from the tetrahedral value by as much as 14°. There are, no doubt, other examples of the phenomenon of large bond angle distortion, but those referred to are sufficiently well established to serve as a basis for further discussion. Since bonds to both metallic and non-metallic atoms such as Pd, As, P, S, N, C and O can be markedly distorted from the ideal values, it is reasonable to assume that bonds to other atoms may, under appropriate conditions, be affected in a similar way. One of the most important implications of the existence of large angle deformations is that bond angles may be so altered as to modify the elements of symmetry of a complex. Before taking up this question, however, the stable ideal configurations will first of all be considered.

QUADRICOVALENT METAL COMPLEXES.

THE CONFIGURATION OF BONDS FREE TO ARRANGE.

The agreement between the results of quantum mechanical investigation of directed valence bonds based on the method of localised pairs developed by Slater, Pauling, and Hultgren and those based on the method of molecular orbitals developed principally by Hund and Mulliken, and the abundant confirmation of these

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* Even if resonance among structures >N–H and >N–H should occur there must still be a large amount of distortion, since the angle >N–H would tend to approach 125°.

theoretical results by experiment, makes it possible to treat the question of deformation of bond angles in more detail than hitherto. Two of the most significant quantum mechanical findings as far as this discussion is concerned are :

  (1) That square coordination is to be expected wherever dsp^2 (or d^2p^2)* orbitals are involved in bond formation.

  (2) That tetrahedral bonding is to be expected when sp^3 orbitals are involved in bond formation.

Any atom whose structure is such as would permit the use of dsp^2 orbitals might, under suitable conditions, be expected to be square rather than tetrahedrally bonded, because dsp^2 bonds are stronger and therefore give rise to more stable complexes than sp^3 bonds. The following is a list of some atoms† for which square coordination is theoretically possible : Co^I, Co^{II}, Fe^{II}, Mn^{II}, Mn^{III}, Ni^{II}, Ag^{II}, Rh^I, Ir^I, Pd^{II}, Pt^{II}, Cu^{II} and Au^{III}. It does not follow that when any one of these atoms exhibits a co-ordination number of four it must of necessity be square coordinated. As an alternative, the metal atom may form four ionic bonds, a circumstance which can, in some instances, be revealed by magnetic susceptibility measurements.‡ It is to be emphasised that the quantum mechanical predictions relating to the directed chemical bond refer only to bonds *free to arrange* as for example in $(Pt(NH_3)_4)^{++}$ and $(PdCl_4)^=$. Bonds free to arrange may, in some instances, assume angles different from the theoretical values of $109° 27'$ (or $90°$) by reason of the fact that the molecules in which they occur resonate between several valence bond structures. Examples of this have been found in the chlorethylenes. Departures of bond angles from theoretical values, arising in this way, are however not included under the term distortion. The

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* A complete survey of all possible stable bond arrangements has been made by G. E. Kimball, *J. Chem. Phys.*, 1940, *8*, 198.

† With regard to claims relating to the square coordination of Pb^{II}, Sn^{II},[7] Tl^I,[3] and Au^I[9] it should be pointed out that dsp^2 bonds cannot be formed by these atoms, and it is not surprising therefore that there is other[10] evidence to show that these atoms are not square bonded. The small cell dimensions (in one direction) of unit cells of certain compounds of Tl^I and Au^I cannot be regarded as satisfactory evidence for the square coordination of these metals.

‡ For a table showing the magnetic moments to be expected for square complexes, see L. Pauling and M. L. Huggins, *Zeit. für Krist.*, 1934, *87*, 214.

origin of the bond angle distortions which form the main concern of this discussion may be sought in the deformation vibrations of bonds. Under suitable conditions the amplitudes of these vibrations may result in two carbon bonds, for example, taking up an angle of 60°, in which position they are locked during the formation of a cyclo-propane molecule. The permanent distortion so produced (permanent in the sense that it persists for the life of the molecule) is inherent in the configuration adopted by the molecule. With the discovery of complexes containing complicated chelate groups, especially quadridentate groups, instances of previously unsuspected and apparently anomalous square and tetrahedral bonding have been brought to light. Many of these may be explained as arising from large bond angle distortions resulting in what may be described as " forced configurations ". While the natural tendency of a metal atom may be to form four bonds directed towards the corners of a tetrahedron or a square, the configuration of a quadridentate chelate may be such as to impose, if it unites with a metal, some sort of a compromise between the natural directions of the bonds of the metal atom and the steric requirements of the organic molecule.* An attempt will be made to classify the different cases which may arise from the opposition of these two factors.

DISTORTED TETRAHEDRAL BONDS.

With rigid planar quadridentate chelate groups such as those found in metallic porphyrin,[11] phthalocyanine[13] and allied derivatives three different types of complex may be formed :

(a) The first comprises complexes in which the central metal atom is held by four square ionic bonds distorted from the tetrahedral configuration of minimum potential energy normally assumed by four ionic bonds free to arrange. The ionic character of the bonds may be investigated in several ways : firstly, by making use of the

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* This implication of the existence of compounds like the metallic phthalocyanine derivatives has already been pointed out by Linstead and Robertson, *Jour. Chem. Soc.*, 1936, 1736, but no detailed and systematic discussion was made of the different possibilities which may arise.

relation suggested by Pauling for determining the amount of ionic character of a bond, viz. :

Amount of ionic character $= 1 - e^{-c(x_A - x_B)^2}$

where x_A and x_B are the electronegativities of the two bonded atoms. This relation can be used to show that the metal-nitrogen bonds in beryllium and magnesium phthalocyanines and in chlorophyll have a large amount of ionic character.

The tests of volatibility and solubility in organic media which have been used[14] to discriminate between ionic and covalent links in metal complexes do not necessarily give reliable indications as the example of nickel bis-acetylacetone will show. The magnetic moment[15] of nickel in this compound shows that it is an ionic* complex, nevertheless the compound is soluble in benzene.

It has been already pointed out that because a d orbital happens to be available for bond formation it does not follow that it will be used. It does not follow, for example, that manganese is square coordinated in manganous phthalocyanine, as has been suggested.[13] Magnetic data are uncertain on the point, chiefly because of some doubt concerning the purity of the compound employed. The measured moment[16] ($\mu = 4 \cdot 9$ Bohr magnetons) lies midway between the value predicted for square coordination ($\mu = 3 \cdot 88$)† and that for ionic binding ($\mu = 5 \cdot 92$).‡ A clear-cut decision can be made for ferrous protoporphyrin, which has been shown to be definitely an ionic complex. Magnetic data are not available for the ferrous, cobaltous, and nickelous derivatives of tetrapyridyl recently described by Morgan and Burstall,[12] but in these complexes there is also a possibility of octahedral coordination. Nevertheless magnetic data will, in favourable cases, distinguish between the various alternatives. The question as to what factors determine whether atoms like Fe, Mn, Co or Ni will form dsp^2 or ionic bonds is an interesting one, but as yet little is known about it. Magnetic studies of cobaltic, ferric, and a wide variety of cobaltous and nickel[17] compounds

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* The term ionic in this context refers to the nature of the bonds to the metal atom of a complex and not, as is more usual, to the fact that the complex as a whole carries a positive or negative charge.

† Orbital contribution should be zero.

‡ Experiments in this laboratory indicate that it is very unlikely that Mn^{II} forms square complexes; at least it does not do so with chelate groups which form square complexes with Ni^{II} and Co^{II}.

suggest that the electronegativity of the atoms bonded to the metal atom plays an important part.

(b) The second type comprises complexes containing a metal atom normally tetrahedral, as for example, zinc, which is tetrahedrally bonded in ZnO,[18] ZnS,[19] $(Zn(CN)_4)^{-2}$[20] and in the zincibenzoylpyruvate ion.[21] The zinc atom in zinc phthalocyanine may be regarded as square bonded under duress. In view of the existence of bond angle deformations amounting to as much as 49° (as in cyclopropane) it is not unreasonable to suppose that tetrahedral sp^3 bonds suffer distortions of about 20° in zinc phthalocyanine. Since neither magnetic data nor bond length measurements are likely to throw any light on the amount of ionic character in the Zn–N bonds of zinc phthalocyanine, the complex might more conservatively be referred to as one in which the Zn–N bonds assume a forced configuration. This conservatism is also warranted by the fact that the act of distortion may well change the amount of ionic character in the Zn–N bond.* The existence of compounds like the zinc, cadmium† and silver‡ derivatives of tetrapyridyl, and the zinc and cadmium porphyrin and phthalocyanine derivatives cannot, in any instance, be taken to imply that these metals will form square bonds when the bonds are free to arrange.

(c) The last type of complex comprises those in which the metal atom forms dsp^2 bonds with little or no distortion as in the phthalocyanine and porphyrin derivatives of Co^{II}, Ni^{II}, Pt^{II}, Pd^{II} and Cu^{II}. The Ni^{II} and Pd^{II} derivatives of both compounds are diamagnetic, which is to be expected for dsp^2 bonding. No clear-cut distinction can be made magnetically between ionically and covalently bound copper. An attempt has been made by L. and W. Klemm[16] to measure the magnetic susceptibility of ferrous and cobaltous phthalocyanines but the results do not permit one to assign these complexes to class (c) with any great certainty. The difficulty with this class of compound is that the preparations involve ferromagnetic starting material. Further work with complexes made under conditions which do not render contamination with ferromagnetic impurities likely is desirable. The moment measured for the ferrous compound is $\mu = 1 \cdot 58 - 1 \cdot 98$,

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* In this connection see the paper which follows.

† Cd^{II} is tetrahedrally bonded in $(Cd(CN)_4)^=$.

‡ Ag^{I} is tetrahedrally bonded in crystalline AgI.

whereas square coordination requires μ to be $2 \cdot 83$. It seems more likely that ferrous phthalocyanine belongs to the class (*a*), involving as it does four Fe^{II}–N bonds similar to those in ferrous protoporphyrin, which is an ionic complex. Cobalt in cobaltous phthalocyanine on the other hand is very probably square coordinated : $\mu = 1 \cdot 93$, the predicted value for dsp^2 bonds is $1 \cdot 73$.*

Distorted Square Bonds.

It is now established beyond all reasonable doubt that quadricovalent Pt^{II}, Pd^{II}, Au^{II} and Ni^{II} (in diamagnetic compounds) form square bonds when these are free to arrange. Evidence from theoretical investigations, from studies of isomerism,[22] crystal structure,[23] optical activity,[24] dipole moments,[25] magnetic susceptibility,[26] Raman spectra[33] and crystal optics[27] all points to this conclusion. Nevertheless some apparent anomalies† still remain. One of these is the existence of the compound β β′ β″ triamino-triethylamine platinous chloride,[28] a complex in which undistorted square coordination is sterically impossible.

Reihlen has quoted this case to prove his contention that platinous compounds are not square coordinated, a conclusion he has also drawn from extensive investigation of the optical activity of platinous complexes.‡[29]

A reasonable interpretation of the structure of this compound is to regard Pt^{II} as tetrahedrally coordinated under duress. That is, just as tetrahedral covalent bonds can be forced to assume a square configuration, so the converse effect, namely distortion of square to tetrahedral bonding, may be expected to occur. The configuration assumed is of course not necessarily a regular tetrahedron. Without exception, Pt^{II} complexes have proved to be

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* There is magnetic evidence that Co^{II} forms square complexes with salicylaldoxime, thiosemicarbazide, and benzylmethylglyoxime : unpublished experiments with D. P. Craig.

† It is improbable that Pt^{II} is ,octahedrally coordinated in this compound. Crystal structure studies definitely show that there are no octahedral complexes in $(Pt(NH_3)_4)Cl_2$ and $(Pd(NH_3)_4)Cl_2$ where they might equally readily have been formed. For further evidence against the view that $(Pt(NH_3)_4)Cl_2$ is an octahedral covalent complex see K. A. Jensen, *Zeit. für anorg u. allg. Chem.*, 1936, *229*, 252.

‡ For an alternative interpretation of this work see a paper by K. A. Jensen, *Zeit. für anorg. Chem.*, 1939, *241*, 115. Jensen concludes that diacido complexes with the bromcamphorsulphonate ion directly attached to platinum are responsible for the observed changes in optical rotation.

diamagnetic ; there is therefore no question of the platinum forming ionic bonds with nitrogen atoms. In view of the results obtained with palladium complexes (described in the next paper) even marked deformation of the Pt^{II}–N bonds is unlikely to render them predominantly ionic in character.
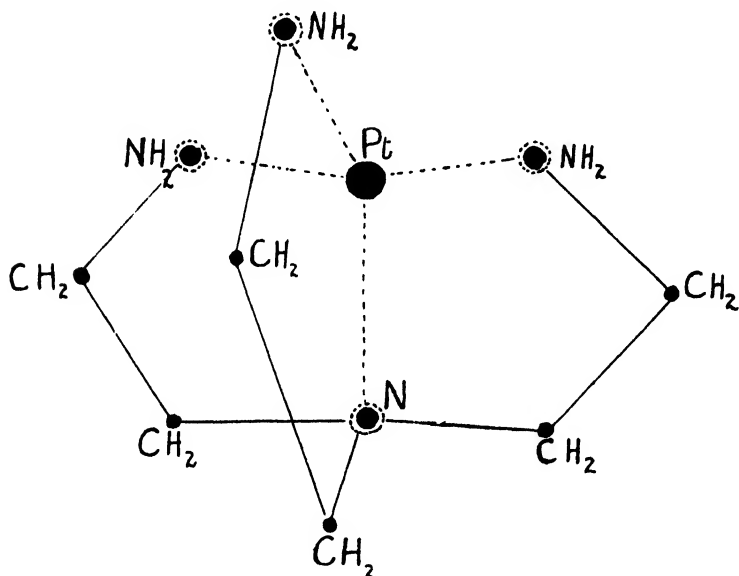

With any chelate group whose configuration is such as to force four bonds to a metal atom to assume a tetrahedral disposition, one of three possible situations may arise. Coordination may occur with

(c) a metal which, when it forms covalent bonds, is square bonded ;

(d) a metal which normally forms tetrahedral (sp^3) bonds ;

(e) a metal which under the circumstances forms ionic bonds.

In the first case only does bond deformation occur. Examples of class (c) additional to, but different from the one already discussed, are to be found among the metal derivatives of certain substituted pyrromethenes. It was Pfeiffer[30] who, when discussing the structure of the copper complex tetramethyl dipyrromethene, first pointed

out that clashing of the methyl groups in positions
(asterisked) will occur if the whole molecule attempts to
assume a planar configuration. It was assumed that
copper exhibited tetrahedral bonding. Since that time,
however, experimental and theoretical investigations have
led to the view that copper, when the four covalent bonds
are free to arrange, assumes a planar configuration.
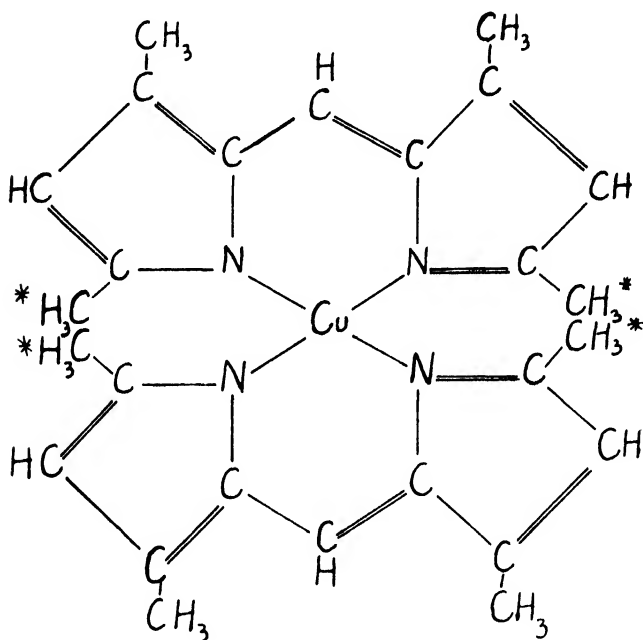
In so far as the electronegativity* of the atoms bonded to
copper is concerned in the formation of covalent bonds,
there can be little doubt that copper forms covalent bonds
with the pyrrole nitrogen atoms in the copper complexes
of phthalocyanine and porphyrins. The copper pyrro-
methene complex may therefore be regarded as one
involving distorted square bonding.† A study of other
metallic derivatives of pyrromethenes has been made by
Porter[31] but without any attempt to classify them. The

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* Copper is square bonded in cupric chloride dihydrate, for example.

† In thus describing the bonding it is not intended to imply that dsp²
orbitals are necessarily concerned in the formation of the metal-
nitrogen bonds.

following metallic derivatives of ethyl $3:3'$ $5:5'$ tetramethylpyrromethene-4 4' dicarboxylate must be assigned to class (c), viz. : nickel, copper, platinum, and palladium and cobalt.

An interesting point which arises in connection with compounds belonging to classes (b) and (d) is this : does the act of distortion affect the character of bonds to the central metal atom ? With some of the metallic pyrromethene derivatives the question whether dsp^2 orbitals are used in forming the distorted bonds or whether the bonds to the metal assume a predominantly ionic character or not can be investigated magnetically. This subject is taken up in the next paper. A further interesting feature of the above pyrromethene complexes is that distortion leads to some bond angles greater than the normal 90°. No marked bond distortion occurs in the zinc and cadmium derivatives of ethyl $3:3'$ $55'$ tetramethylpyrromethene $4:4'$ dicarboxylate consequently these may be assigned to class (d). In regard to class (f) certain difficulties arise. If the act of distortion produces a change from a covalent bond to one predominantly ionic in character, then no distinction can be drawn between (d) and (f). On the other hand a metal like magnesium which forms ionic bonds to nitrogen (see electronegativity difference criterion) would be expected to form a complex of type (f). In point of fact, Porter was unable to prepare either the magnesium or beryllium derivatives of pyrromethenes. In the great majority of cation complexes where Ni^{II} is bonded to four nitrogen atoms the magnetic criterion shows the Ni^{II}–N bonds are predominantly ionic. For this reason it is quite probable that paramagnetic β β' β'' triamino triethylamine nickel thiocyanate ($\mu = 2 \cdot 8$ Bohr magnetons) belongs to class (e), although an octahedral configuration is not excluded by the magnetic data[32].

Other forced configurations are conceivable, but they are not of much significance in relation to the stereochemistry of the metals : three pyramidal bonds might be distorted to planar triangular configuration* and two collinear bonds

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* It is conceivable that three normally pyramidal[3], [35] single bonds to nitrogen could be forced into a plane if for example the nitrogen atom became a common member of two plane and coplanar rings. Three coplanar bonds to nitrogen in this situation do occur in nickel phthalocyanine[36] (isoindole nitrogen atoms) and in the cyamelurate[37] ion (where nitrogen is common to three rings) but in these instances

to a bent configuration. As an example of the latter the silver salt of 34' dinitro diazoaminobenzene[34] may be mentioned. Normally, bicovalent silver forms linear complexes as in $(Ag(CN)^2)^-$ but when silver is attached to two nitrogen atoms of the triazene group distortion of the two bonds to silver must occur.

SUMMARY.

Baeyer's assumption that the angle between the valence bonds of carbon can be widely altered from the normal tetrahedral value (109° 27') can be extended to the valence bonds of many other atoms including those forming bonds normally at 90° as well as those of the tetrahedral class. The significance of this for the stereochemistry of the quadricovalent metals and the usefulness of the magnetic criterion in determining bond types in distorted complexes are discussed.

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[*Continuation of footnote from previous page.*]
the planar configuration can be attributed to resonance.[38] The bonds to nitrogen are not single bonds : each bond has some double bond character. It is clear that the criterion set up by Kenner and Jackson[39] for proof of the coplanar configuration of tervalent nitrogen is inadequate.

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MAGNETIC STUDIES OF COORDINATION COMPOUNDS.

PART II. THE EFFECT OF DISTORTION OF VALENCE BOND ANGLES IN NICKEL AND PALLADIUM DERIVATIVES OF SUBSTITUTED PYRROMETHENES.[*]

By D. P. MELLOR, M.Sc.,

and W. H. LOCKWOOD, B.Sc.

In selecting test cases for investigating the effect of distortion of valence bond angles on bond character, it is obviously necessary to choose substances in which the bonds to be studied are such as will assume well established orientation when they are free to arrange. For example, it is well known that four covalent bonds to nickel are normally coplanar and that complexes containing such bonds are diamagnetic. This correlation between structure and magnetic properties has been established in a number of different ways : by the discovery of isomeric nickel glyoximes,[1] crystal structure determinations (potassium nickel dithio-oxalate),[2] and by investigations relating to crystal optics[3] and isomorphism[4] of other diamagnetic nickel compounds. Among the many diamagnetic nickel complexes which have been described, those internal complexes in which four nitrogen atoms are bonded to the metal atom are of special interest for the present investigation. The complete X-ray determination of the structure of nickel phthalocyanine[5] has firmly established the coplanar character of the bonds between the nickel and the four pyrrole nitrogen atoms. Both nickel phthalocyanine[6] and nickel protoporphyrin[7] are diamagnetic. It can, therefore, be assumed that other nickel complexes in which the metal is bonded to four pyrrole nitrogen atoms in such a way that the metal bonds are free to adopt their normal

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configuration, will prove to be diamagnetic.* A similar argument can be developed for palladous compounds for which there is ample evidence of square coordination. All palladous compounds in which square bonding has been established are diamagnetic.

Porter[8] has shown that when certain substituted pyrromethenes with methyl groups in α positions (*e.g.*, ethyl 33′ 55′ tetramethyl pyrromethene 44′ dicarboxylate, Fig. 1A)
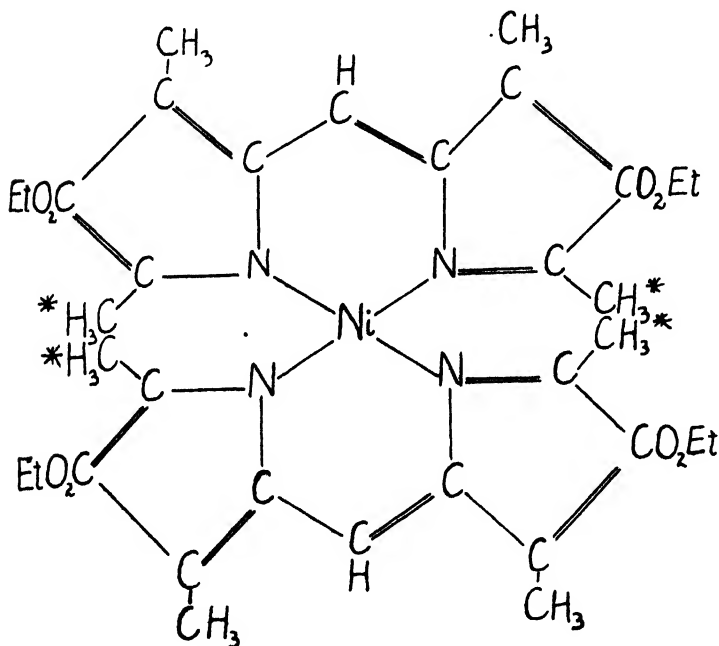

Fig. 1A.

function as chelate groups and attempt to assume a planar configuration, as with palladium and nickel, clashing between the methyl groups must occur. This clashing is perhaps more serious than would be gathered from Porter's diagram. In redrawing it (Fig. 1B) the methyl groups have been given a van der Waals radius of 2 A.U. If it is borne in mind that the van der Waals thickness of the

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* In point of fact, all internal nickel complexes in which nickel is bonded to four nitrogen atoms irrespective of whether these nitrogen atoms belong to pyrrole rings, oxime, or triazene groups have proved to be diamagnetic.

pyrrole rings is somewhere in the neighbourhood of
3·5 A.U., it can be seen that the marked overlapping of
the α methyl groups (indicated by horizontal shading)
implies a very extensive steric effect. It should be pointed
out that, owing to resonance in the pyrrole ring, the α
methyl groups would normally be coplanar with the ring.
Under stress the methyl groups may be bent to some small
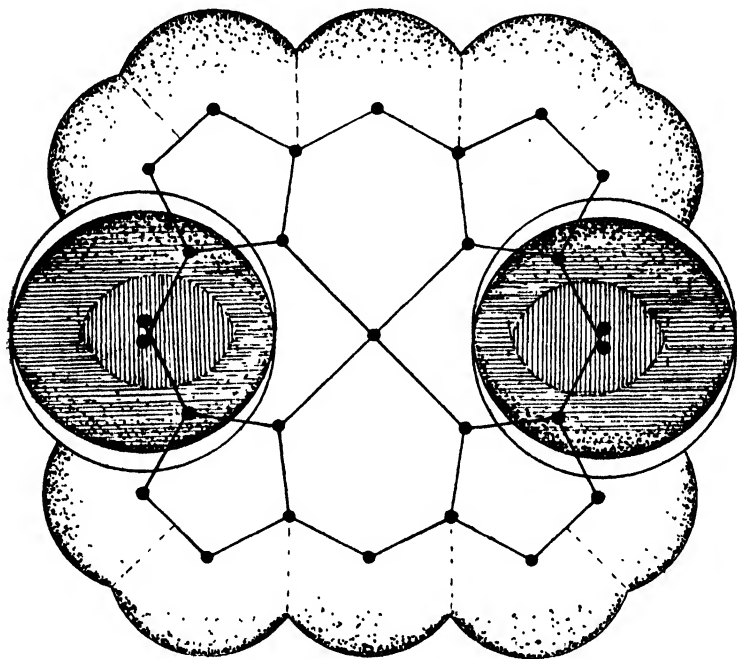extent out of the plane of the pyrrole ring, and it is probable

Fig. 1B.

that the resulting configuration of the complex is a com-
promise between two tendencies—that of the nickel bonds
to assume a square configuration and that of the C–CH$_3$
bonds to remain in the plane of the pyrrole rings and the
steric effects of the clashing methyl groups. Owing
to the large van der Waals radius of the methyl groups no
amount of distortion of the C–CH$_3$ bonds could
accommodate chelating pyrromethene groups in square
coordinated positions. Most of the distortion, therefore,
must occur among the metal-nitrogen bonds. The sub-
stances chosen for the purpose of magnetic investigation

were the nickel and palladium derivatives of ethyl 33' 55' tetramethyl pyrromethene 44' dicarboxylate.

EXPERIMENTAL.

Preparation of 33' 55' Tetramethyl 44 Dicarbethoxy Dipyrromethene and its Nickel and Palladium Derivatives.[9]

Acetoacetic ester (60 gm.) and acetic acid (135 gm.) in a flask provided with a stirrer were cooled in a freezing mixture. Sodium nitrite (16 gm.) was dissolved in the minimum of water and cooled to $0°$ C. and then added slowly, care being taken that the temperature did not rise above $4°$ C. After all the nitrite had been added, the reaction mixture was stirred for a further half hour. The flask was then removed from the freezing mixture and Zn dust (30 gm.) added at sufficient rate to keep the solution boiling. The mixture was heated on a sand bath for one and a half hours and then poured into $1\frac{1}{2}$ litres of water. The crude $2:4$ dimethyl $3:5$ dicarbethoxy-pyrrol separated out; yield 32 gm. It was sufficiently pure for half saponification.

The ester was suspended in 10% alcoholic potash and refluxed for two hours. It was then poured into a litre of water and the unchanged diester filtered off. The $2:4$ dimethyl 3-carbethoxy-pyrrol 5 carboxylic acid was obtained by acidification with acetic acid; yield 25 gm. The crude product was sufficient for the dry distillation.

The half ester was put into a small distillation flask and heated till the evolution of CO_2 had almost ceased. It was then distilled under 28 mm. Hg. The white and crystalline product was recrystallised from kerosene; yield 10 gm., M.P. $75\cdot3-75\cdot8$.

Two grams of the α-free pyrrol were dissolved in concentrated hydrochloric acid and excess formic acid added. The mixture was heated for ten minutes on the boiling water bath and then allowed to stand for two hours in the ice chest. The fine red needles of 33' 55' tetramethyl 44' dicarbethoxydipyrromethene were filtered off. This, after washing with 10% HCl, was suspended in about 100 c.c. alcohol and about 5 c.c. saturated sodium acetate added. On warming and adding $1\cdot5$ gm. nickelous acetate dissolved in the minimum of hot water the dipyrromethene hydrochloride dissolved and the solution darkened. On cooling strongly pleochroic rhomboidal plates of the nickel complex separated and these were recrystallised from alcohol.

Analysis of nickel complex. Found: Ni $=7\cdot98\%$, N $=7\cdot52\%$. Calculated for Ni $(C_{38}H_{46}O_8N_4)$: Ni $=7\cdot88\%$, N $=7\cdot51\%$.*

The palladium complex was prepared by adding palladous nitrate (1 mol.) dissolved in water to the base (2 mols.) with excess of sodium acetate in alcohol.[8] This procedure avoids the formation of binuclear complexes which may occur when potassium chloropalladite is used as a starting material. The substance separated as a microcrystalline brick red powder together with a small amount of palladium from which it was separated by several recrystallisations from chloroform. Analysis of palladium complex: N $= 7\cdot2\%$. Calculated for $Pd(C_{38}H_{46}O_8N_4)$: N $=7\cdot1\%$.†

Magnetic Susceptibility Measurements.

These were carried out by the usual Gouy method and the following results were obtained.

Substance.	$\chi \ 10^{-6}$.	$\chi M \times 10^{-6}$.	μ (Bohr Magnetons).
$Ni(C_{38}H_{46}O_8N_4)$	$+5\cdot14$	$+4258$	$3\cdot2$
$Pd(C_{38}H_{46}O_8N_4)$	$-0\cdot7$	Diamagnetic	$0\cdot0$

Discussion of Results.

Susceptibility measurements show clearly that the nickel complex is paramagnetic. The nickel atom has a moment of $3\cdot2$ Bohr magnetons which, after allowing for a small orbital contribution, corresponds to the existence of two unpaired electron spins. From this it may be inferred that forcing the nickel-nitrogen bonds out of the normal square configuration profoundly alters their character: they are no longer essentially covalent bonds involving the use of dsp^2 orbitals, but are predominantly ionic in character. It is a matter of some interest to determine qualitatively how much distortion is required to change the character of the nickel bonds. From Fig. 1

* These analyses were carried out by Dr. G. Burger, of the University of Adelaide.

† We are indebted to Miss D. Little for carrying out this analysis.

it can be seen that some small distortion must occur even when hydrogen atoms replace the α methyl groups : vertical shading indicates the overlap of α hydrogen atoms. It is hoped eventually to study compounds with hydrogen atoms in α positions and also compounds in which two (of the four) α methyl groups are replaced by hydrogen atoms. In view of the fact that all palladous compounds so far investigated have proved to be diamagnetic[10] the significance of the results obtained with the palladium complex is not clear. Further discussion of the problem may be possible when the moment of palladium in PdF_2 is known. This compound of palladium (Pd^{II}) with the most electronegative of all elements is the one most likely to be paramagnetic. If PdF_2 should prove to be diamagnetic, the failure of mere deformation of palladium nitrogen bonds to produce ionic palladium will not be surprising. On the other hand, if PdF_2 should prove to be paramagnetic (and its crystal structure, which is very different from that of $PdCl_2$, indicates that it may well be so) then the result obtained in the present investigation simply indicates that the Pd–N is so much more stable than the corresponding nickel bond that its character is unchanged by deformation. In this connection it should be pointed out that the palladium derivative is much more stable than the nickel derivative towards hydrochloric acid.[8]

ABSORPTION SPECTRA.

The metal derivatives of ethyl 33′ 55′ tetramethyl-pyrromethene 44′ dicarboxylate are characterised by a narrow band in the region of 5,000 A.U. If one plots the position of the maximum of this band against atomic number for the series Co, Ni, Cu, and Mn, it is found that after rising to a maximum at copper there is a marked drop to zinc.

Of this series the zinc complex is the only one in which marked valence bond angle deformation does not occur, since zinc normally forms tetrahedral (sp^3) bonds. Insufficient is known about the relation between structure and absorption for complexes of this type to enable one to attach any special significance to the above observation.*

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* The palladium complex has a narrow band in the region 4864 ($\pm 3 \cdot 6$ A.U.) : private communication from Mr. J. Legge.
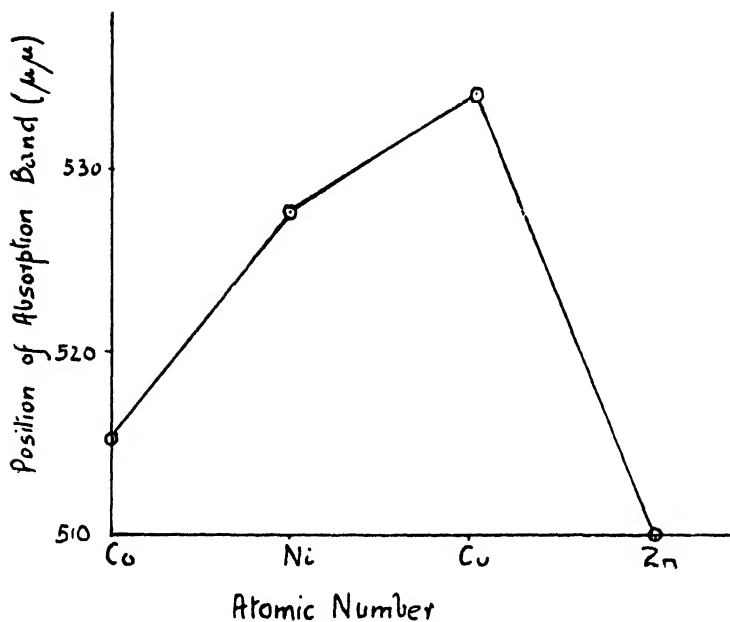
Fig. 2.

Data for this diagram were taken from a paper by
Fischer and Schubert.[10]

SUMMARY.

Magnetic studies of palladium and nickel derivatives of
a suitably substituted dipyrromethene show that large
distortion of bond angles may profoundly alter bond
character. This is true for the nickel complex when the
metal bonds change from covalent to predominantly ionic
but no change in character occurs with palladium.

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THE SEGRE QUARTIC SURFACE WITH FOUR NODES.

By T. G. ROOM, M.A.

A circular cylinder in space of four dimensions[1] is the locus of planes absolutely parallel to, and at a constant distance from, a fixed plane, the axial plane. The surface with which this note is concerned is the meet of two such cylinders, with equal radii, and absolutely perpendicular axial planes.[2] Consideration of this surface was first suggested by its close relation to Goddard's surface[3], which is, in fact, an orthogonal projection of it, and its intrinsic interest justified a deeper study. Among the more noteworthy properties of the surface are those expressed in the following theorems :

(i) the surface can be straightened out into a plane,

(ii) the surface has on it a pair of orthogonal families of circles and a pair of orthogonal families of ellipses, the curves of all four families being geodesics,

(iii) projectively the surface is the intersection of two quadric line-cones in general position,

(iv) the birational representation of the surface on a plane cannot be effected by cubic curves if real points are to correspond to real points.

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[1] A space of n dimensions will be denoted by $[n]$, and a $[3]$ will be referred to as a *solid*.

[2] Two absolutely parallel planes in $[4]$ lie in the same solid, and are parallel in that solid in the ordinary sense : two planes in $[4]$ with a single common point which is at infinity are parallel in a weaker sense. Two absolutely perpendicular planes are such that all directions in each are perpendicular to all directions in the other. There is a weaker type of perpendicularity (the only type possible in $[3]$) in which only one direction in each plane is perpendicular to all directions in the other.

[3] Goddard, *Proc. Roy. Soc. N.S.W.*, 1939, **73**, 107–111. Plate showing a model of the surface faces p. 110.

1. EQUATIONS OF THE SURFACE; CIRCLES AND ELLIPSES.

Denote by H the surface under consideration, and by Γ and Δ the two cylinders, of radius a, by which it is defined. Each generating plane $\{\gamma\}$ of Γ cuts Δ in a circle γ of radius a whose centre lies in the axial plane of Δ, and on the circle, also of radius a, in which that plane cuts Γ. There is an identical family of circles δ in the generating planes $\{\delta\}$ of Δ. Thus H can be constructed, and that in two distinct ways, as the locus of circles of radius a whose centres lie on a circle of radius a, and whose planes are absolutely perpendicular to the plane of that circle; it might be visualised as a somewhat tenuous torus.

If the axial planes of Γ and Δ are taken to be $y=0$, $z=0$, and $x=0$, $t=0$, the equations of Γ and Δ are:

$$\Gamma \qquad x^2+t^2=a^2 \tag{1.1}$$
$$\Delta \qquad y^2+z^2=a^2 \tag{1.2}$$

All the quadrics of the family
$$x^2+t^2-a^2+\varkappa(y^2+z^2-a^2)=0$$
pass through H, and among them is the point-cone Φ, with vertex at the origin,

$$\Phi \qquad x^2-y^2-z^2+t^2=0 \tag{1.3}$$

Φ has on it two real families of planes, $\{\alpha\}$ and $\{\beta\}$, viz.:

$$\{\alpha\} \qquad x+y=\alpha(z+t), \quad x-y=\alpha^{-1}(z-t)$$
$$\{\beta\} \qquad x+y=\beta(z-t), \quad x-y=\beta^{-1}(z+t),$$

which cut the cylinders, and therefore also the surface H, in conics, α and β say, which, since the cylinders are circular, must be ellipses. From their equations it is easy to see that the planes $\{\alpha\}$ with parameters α and $-\alpha^{-1}$ are absolutely perpendicular, i.e., the planes of each family form an involution of perpendicular pairs, and, further, any solid through a plane $\{\alpha\}$ cuts Φ in a plane $\{\beta\}$ which is perpendicular in the ordinary three-dimensional sense to $\{\alpha\}$.

From equations 1.1 and 1.2 we can deduce a simple parametric form for the surface, viz.:

$$x=a\cos\lambda, \ y=a\cos\mu, \ z=a\sin\mu, \ t=a\sin\lambda \tag{1.4}$$

where $0 \leqslant \lambda, \ \mu \leqslant 2\pi$. The circles γ and δ are the loci of points for which respectively μ and λ are constant. An ellipse α is given by the values of λ, μ which satisfy

$$\cos\lambda+\cos\mu=\alpha(\sin\lambda+\sin\mu),$$

i.e., $\qquad \cot\tfrac{1}{2}(\lambda+\mu)=\alpha.$

It is therefore the locus of points for which $\lambda+\mu$ is constant. Similarly along an ellipse β, $\lambda-\mu$ is constant.

2. The Application of the Surface to a Plane.

Using the parameters λ, μ of equations 1·4, we find for the arc-element of the surface H

$$ds^2 = d\lambda^2 + d\mu^2.$$

H is therefore applicable to a plane (Theorem I). The application can be effected in two stages. First the cylinder Γ can be cut along a generating plane, and flattened out into a complete solid, which may be taken to be $t=0$. When this is done H is deformed into the part of the cylinder

$$y^2 + z^2 = a^2$$

which lies between $x=0$ and $x=2\pi a$. Secondly this cylinder may be straightened into the part of the plane ($z=0$ say) for which $0 \leqslant x < 2\pi a$, $0 \leqslant y < 2\pi a$. Points of the lines $x=2\pi a$, and $y=2\pi a$ are derived from the same points on H as are the corresponding points on $x=0$, and $y=0$. For clarity we use ξ, η instead of x, y for coordinates; the direct algebraic representation of the surface is then obtained from equations 1·4 and $\xi = a\lambda$, $\eta = a\mu$.

The circles γ and δ are transformed into segments of lines parallel to the ξ and η axes, and the conics α and β into lines parallel respectively to $\xi + \eta = 0$, and $\xi - \eta = 0$.[4] Since all these curves deform into straight lines, they must be geodesics on the original surface, and, further, since the angles between curves are unchanged in the deformation, all circles α are orthogonal to all β, and all ellipses γ to all δ. (Theorem II.)

3. The Projection of the Surface into Goddard's Surface.

Transform the equations 1·4 by making the substitutions

$$\sqrt{2}x' = x - y, \quad \sqrt{2}y' = x + y, \quad \sqrt{2}z' = z + t, \quad \sqrt{2}t' = z - t,$$
$$(3 \cdot 1)$$
$$\theta = \tfrac{1}{2}(\lambda + \mu), \quad \varphi = \tfrac{1}{2}(\mu - \lambda), \quad c = \sqrt{2}a \qquad (3 \cdot 2)$$

We obtain

$$x' = c \sin \theta \sin \varphi, \quad y' = c \cos \theta \cos \varphi, \quad z' = c \sin \theta \cos \varphi,$$
$$t' = c \cos \theta \sin \varphi.$$

Goddard's surface, G, is represented by the first three of

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[4] In general parts of two lines are required to represent a whole ellipse. E.g., if $0 < h < 2\pi a$, the ellipse corresponding to $\xi + \eta = h$ is represented by this line between the points $(0, h)$ and $(h, 0)$, and by the line $\xi + \eta = h + 2\pi a$ between $(2\pi a, h)$ and $(h, 2\pi a)$.

these equations,[5] and is therefore the orthogonal projection of H on to $t'=0$. It may be remarked further that identical surfaces are obtained by orthogonal projection on to all solids $x'+kt'=0$, and $y'+k'z'=0$. Thus, write $x''=x'\cos\psi+t'\sin\psi$, $t''=-x'\sin\psi+t'\cos\psi$, $\theta'=\theta+\psi$, and we obtain $x''=\sin\theta'\sin\varphi$, etc. Then project on to $t''=0$, i.e., on to $x'-t'\cot\psi=0$.

Referred to the $x'y'z't'$ coordinate system the equation of the two cylinders are:

$\Gamma \quad (x'+y')^2+(z'-t')^2=c^2$

$\Delta \quad (x'-y')^2+(z'+t')^2=c^2$

and the cone is

$\Phi \quad x'y'-z't'=0$.

For convenience we shall use $(x, \bar{y}, \bar{z})$ for the point which is the projection of (x', y', z', t'), so that formally $\bar{x}=x'$ $\bar{y}=y'$, $\bar{z}=z'$. The equations of a plane $\{\gamma\}$ are:

$$x'-y'=c\cos\mu, \quad z'+t'=c\sin\mu,$$

and the solid through it parallel to Ot' is

$$x'-y'=c\cos\mu.$$

This solid cuts the cylinder Γ residually in a second plane, $\{\gamma\}$, viz.:

$$x'-y'=c\cos\mu, \quad z'+t'=-c\sin\mu.$$

These two planes project into the same plane in $t'=0$, thus the planes of the family

$$\bar{x}-\bar{y}=c\cos\mu,$$

cut G in pairs of ellipses. If $\mu=0$, or π, these two planes coincide (the solids $x'-y'=\pm c$ are tangent to Γ), and provide two of the tropes on G.[6] Circles δ on H project similarly into pairs of coplanar ellipses, and provide the other two tropal conics.

On the cone Φ there is one plane $\{\alpha\}$ and one $\{\beta\}$, say $\{\alpha_0\}$ and $\{\beta_0\}$, parallel to Ot', namely the coordinate planes $y'=0$, $z'=0$, and $x'=0$, $z'=0$. Thus the solid through any plane $\{\beta\}$ parallel to Ot' cuts Φ residually in $\{\alpha_0\}$. On projection the two conics α_0, β_0 provide the two double lines, $\bar{\alpha}_0$, $\bar{\beta}_0$[7] and the planes through $\bar{\alpha}_0$, and $\bar{\beta}_0$ cut G residually in ellipses which are the orthogonal projections of the ellipses β and α.

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[5] Goddard, *l.c.*, p. 110.

[6] Goddard, *l.c.*, p. 111.

[7] Goddard, *l.c.*, p. 110.

4. The Mapping of Goddard's Surface on a Square.

The representation of H discussed in §2 provides also a mapping of G, which, however, is neither a conformal representation, since the orthogonal projection involves distortion, nor a birational representation, since the mapping is repeated in every square

$$2n\pi a \leqslant \xi, \quad \eta < 2(n+1)\pi a.$$

Collating the results of §§2, 3, we find the following main features in the mapping :

Tropes→lines $\xi = 0$, $\xi = \pi a$, $\eta = 0$, $\eta = \pi a$.

Synclastic parts of the surface→$0 < \xi < \pi a$, $0 < \eta < \pi a$; $\pi a < \xi < 2\pi a$, $\pi a < \eta < 2\pi a$.

Double line, $x = 0$, $z = 0$→line, l, $\xi + \eta = 2\pi a$, between $(0, 2\pi a)$ and $(2\pi a, 0)$; $(\xi, 2\pi a - \xi)$, and $(2\pi a - \xi, \xi)$ represent the same point in space.

Double line, $\bar{y} = 0$, $\bar{z} = 0$→lines, m, $\xi - \eta = \pi a$ between $(\pi a, 0)$ and $(2\pi a, \pi a)$, and m', $-\xi + \eta = \pi a$ between $(0, \pi a)$ and $(\pi a, 2\pi a)$.

Part of the surface for which $\bar{z} > 0$ — the part of the square which is to the left of l and between m and m', together with the parts to the right of l, and outside m and m'.

5. Projective Representations of the Surface on a Plane.

The projective model, Π, of H is the meet of two quadric line-cones in [4], and is therefore a special Segre quartic surface,[8] for which, of the five point-cones in the pencil of quadrics through the surface, four are replaced by the two line-cones. To find a simple form for the equations of these line-cones, let the vertices of the two cones be XT and YZ, the points X, Y, Z, T being those in which the vertex of one cone meets the other cone. The solid $XYZT$ has a definite polar plane with regard to each of the cones, and these two planes have a single common point, S say. Referred to $XYZTS$ as simplex of reference, and with a suitable unit point, the equations of the cones take the form

$$\Gamma : \quad xt = s^2$$
$$\Delta : \quad yz = s^2.$$

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[8] Baker, " Principles of Geometry ", Vol. 4 (Cambridge, 1925), Chapter 6. The general Segre quartic surface is discussed in this chapter, and some properties of the special surface Π are given on pp. 196-8.

The point-cone of the system is

$$\Phi : \quad xt - yz = 0.$$

The surface Π has four double points, namely X, Y, Z, T, and there are on it, instead of the usual 16 lines, only four lines, namely XY, XZ, TY, TZ. Likewise instead of the ten families of conics on the general Segre surface, there are only four families, one in the planes of each of Γ and Δ, and two in those of Φ.

We can distinguish projectively four main types of surfaces, if account be taken of the reality of the four double points, the four lines, and the vertices of the two cones, namely (using " p.c.i." for " pair(s) of conjugate imaginary ") :

	Π_0.	Π_1.	Π_2.	Π_3.
Double points	4 real	1 p.c.i. 2 real	2 p.c.i.	2 p.c.i.
Lines ..	4 real	2 p.c.i.	2 p.c.i.	1 p.c.i. 2 real
Cone-vertices	2 real	2 real	2 real	1 p.c.i.

Of these Π_2 has the same real elements as H.

Corresponding to these the equations of the cones may be taken to be :

	Γ	Δ	Φ	Double points.
Π_0	$xt = s^2$	$yz = s^2$	$xt = yz$	X, Y, Z, T
Π_1	$xt = s^2$	$y^2 + z^2 = s^2$	$xt = y^2 + z^2$	$X, T, Y \pm iZ$
Π_2	$x^2 + t^2 = s^2$ ..	$y^2 + z^2 = s^2$	$x^2 + t^2 = y^2 + z^2$	$X \pm iT, Y \pm iZ$
Π_3	$(x + iy)(z - it) = s^2$	$(x - iy)(z + it) = s^2$	$xt = yz$	$X \pm iY, Z \pm iT$

If $s = 0$ be taken to be the solid at infinity, and $(ax/s,\ ay/s,\ az/s,\ at/s)$ orthogonal cartesian coordinates,

Π_2 is identical with H, i.e., regarded projectively, H is the meet of two quadric line-cones in general position (Theorem III).

In the customary plane representation of the general Segre quartic surface solid sections correspond to cubic curves through five fixed points, the correspondence being established by direct projection from a line on the surface.[9] We expect therefore to get a representation of this type in which real points correspond to real points only for Π_0 and Π_3, on which there are real lines. For Π_0, using u, v, w as coordinates in the plane, we obtain one representation by way of the equations[10]

$$x : y : z : t : s = u^2v : v^2u : w^2u : w^2v : uvw.$$

Solid sections are represented by cubic curves touching VW and UW at V and U respectively, and passing through W. The other main features of the representation are:

Line $XY \rightarrow$ line UV.
Lines ZT, XZ, $YT \rightarrow$ points W, U, V.
Conics γ, δ in planes of Γ, $\Delta \rightarrow$ lines through V, U.
Conics α, β in planes of $\Phi \rightarrow$ lines through W, and conics touching VW, UW at V, U.
Double points X, $Y \rightarrow$ points U, V.
Double points Z, $T \rightarrow$ lines UW, VW.

There is only one way in which the base system can be made to include pairs of conjugate imaginary elements and at the same time define a family of real cubic curves, namely, by taking one pair of conjugate imaginary points and one real point, and making the cubic curves pass through these and have at the conjugate imaginary points fixed conjugate imaginary tangents. If the points are $U \pm iV$, W, and the tangents are $u^2 + v^2 = 0$, the equations of the correspondence are

$$x : y : z : t : s = u(u^2 + v^2) : v(u^2 + v^2) : uw^2 : vw^2 : w(u^2 + v^2)$$
$$(5 \cdot 2)$$

The equations resulting from the elimination of u, v, w among these equations are those of Π_3, and thus Π_2, and therefore also H, cannot be represented on a plane by real cubic curves (Theorem IV).

An alternative representation of Π_0 is obtained by a reciprocal inversion transformation in which two of the

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[9] Baker, *l.c.*, p. 165.

[10] This may be regarded as a projection from ZT on to XYS.

base points are U and V. In its simplest form the result of the transformation is to give for the equations

$$x : y : z : t : s = u(u-w)(v-w)^2 : v(v-w)(u-w)^2 :$$
$$u^2v(v-w) : v^2u(u-w) : uv(u-w)(v-w)$$
$$(5\cdot3)$$

The prime sections are represented by quartic curves which have fixed double points at U and V, and fixed simple points at $V+W$, $W+U$, W, $U+V+W$.

Complex systems defining real curves can be derived from this system in two ways : (i) by taking the double points to be real, and the simple points to be two pairs of conjugate imaginary points, e.g., U, V, and $\pm iU \pm iV+W$. The system so defined is

$$x : y : z : t : s = (w^2-u^2)(w^2+v^2) : (w^2-v^2)(w^2+u^2) :$$
$$2vw(w^2+u^2) : 2uw(w^2+v^2) : (w^2+u^2)(w^2+v^2)$$
$$(5\cdot4)$$

These correspond to Π_2

(ii) By taking two of the simple points real, and the remaining points as two pairs of conjugate imaginaries, e.g., W, $U+V+W$, $U\pm iV$, $U+W\pm i(V+W)$. The curves defined are the system of " bicircular " quartics derived from the system of " circular " cubics by a circular inversion with regard to the circle centre $U+V+W$ of radius $\sqrt2$. The system represents Π_3 again.[11]

The surface Π_1 cannot be fitted into this scheme, but there is an alternative representation of Π_0 by real binodal quartics which can be modified to accommodate it, namely :

$$x : y : z : t : s = u^2v(v+w) : u^2vw : uw(v+w)^2 :$$
$$vw^2(v+w) : uvw(v+w).$$
$$(5\cdot5)$$

The solid sections are represented by quartic curves which have double points at U and V, the tangents at U being fixed (namely, $v=0$, $v+w=0$), and the residual intersections of these tangents with the curve fixed and collinear with V (namely, the points W, $V-W$). If the fixed tangents at U are taken to be conjugate imaginary lines (say $v^2+w^2=0$),

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[11] The deceptively simple scheme

$$x : y : z : t : s = u^2(v^2-w^2) : 2u^2vw : w^2(v^2-w^2) : 2vw^3 : uw(v^2+w^2),$$

which certainly leads to bicircular quartics, and, on elimination of u, v, w, to the equations of Π_3, does not provide a (1, 1) representation, since the same point on the surface corresponds to the two points (u, v, w) and $(u/w, w/v, -1)$ in the plane.

the fixed simple points being then $V \mp iW$, we obtain a representation of Π_1, namely

$$x : y : z : t : s = u^2(v^2+w^2) : uw(v^2-w^2) : 2uvw^2 :$$
$$w^2(v^2+w^2) : uw(v^2+w^2).$$
$$(5 \cdot 6)$$

6. A Cartesian Form of the Projective Representation of Goddard's Surface.

To change from the projective to the Cartesian coordinate system, take as the Cartesian coordinates x, y, z, t of §§1–3 the ratios ax/s, ay/s, az/s, at/s of the homogeneous system. The Cartesian representation of §3 expressed in equations $1 \cdot 4$, $3 \cdot 1$, $3 \cdot 2$ then connects with the projective representation expressed in equations $5 \cdot 4$ by way of the relations

$$\tan \tfrac{1}{2}\lambda = u/w, \ \tan \tfrac{1}{2}\mu = v/w$$

among the parameters. The resulting equations of H are, in the x', y', z', t' coordinates :

$$x' : y' : z' : t' : c = (u^2-v^2)w^2 : w^4-u^2v^2 :$$
$$w(u-v)(w^2-uv) : w(u+v)(w^2+uv) : (u^2+w^2)(v^2+w^2)$$

Goddard's surface, the orthogonal projection of H on to $t'=0$, is represented by these equations with t' and the function corresponding to it omitted. To put these equations in Cartesian form, write $\xi'=u/w$, $\eta'=v/w$. The equations of G are then

$$\bar{x} : \bar{y} : \bar{z} : c = \xi'^2-\eta'^2 : 1-\xi'^2\eta'^2 :$$
$$(1-\xi'\eta')(\xi'-\eta') : (1+\xi'^2)(1+\eta'^2).$$

The plane sections of G are represented by quartic curves having double points at the points at infinity on the axes, and a simple point at each of the four complex points $(\pm i, \pm i)$. The equations of the two pairs of asymptotes to the curve representing the section by the plane $\bar{l}x + m\bar{y} + n\bar{z} - p = 0$ are :

$$(p+m)\xi'^2 - n\xi' + p + l = 0$$
$$(p+m)\eta'^2 + n\eta' + p - l = 0.$$

The sum of the four roots of these equations is zero, and thus the system of curves representing plane sections of G is the subsystem of that representing solid sections of H, defined by the property that the sum of the distances of the four asymptotes from the axes to which they are parallel is zero.

There are four families of planes which cut G in pairs of conics (§3), special members of the families providing the tropes. The representations are :

Plane $\bar{x}-\bar{y}=c(h^2-1)/(h^2+1)\rightarrow$pair of lines $\xi'^2-h^2=0$.

Trope $\bar{x}-\bar{y}=-c\rightarrow$line $\xi'=0$.

Trope $\bar{x}-\bar{y}=c\rightarrow$point at infinity on the η'-axis.

Plane $\bar{x}+\bar{y}=-c(k^2-1)/(k^2+1)\rightarrow$ pair of lines $\eta'^2-k^2=0$.

Trope $\bar{x}+\bar{y}=c\rightarrow$line $\eta'=0$.

Trope $\bar{x}+\bar{y}=-c\rightarrow$point at infinity on the ξ'-axis.

Plane $\bar{y}=\alpha\bar{z}\rightarrow$rectangular hyperbola $(\xi'+\alpha)(\eta'-\alpha)=-\alpha^2-1$.

Double line $\bar{y}=0$, $\bar{z}=0\rightarrow$rectangular hyperbola $\xi'\eta'=1$, (points $(\xi', 1/\xi')$ and $(-\xi', -1/\xi')$ represent the same point on the surface).

Plane $\bar{x}=\beta\bar{z}\rightarrow$rectangular hyperbola $(\beta\xi'+1)(\beta\eta'+1)=\beta^2+1$.

Double line $\bar{x}=0$, $\bar{z}=0\rightarrow$line $\xi'-\eta'=0$ (points (ξ', ξ') and $(-\xi', -\xi')$ represent the same point on the surface).

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EXPERIMENTS ON THE SYNTHESIS OF THE PYRIDINE ANALOGUE OF VITAMIN B₁ (ANEURIN).

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(Manuscript received, November 22, 1939. Read, July 3, 1940.)

The experiments described in this paper were originally undertaken because it was thought that 2-methyl-3-(β-hydroxy-ethyl)-N-((2-methyl-6-amino-pyrimidyl-(5)-methyl)-pyridinium chloride hydrochloride (I)* — the pyridine analogue of aneurin (II)—might possess a physiological action similar to that of the vitamin itself; and, if so, might throw some light on its mode of action in the body. The synthesis of compounds structurally
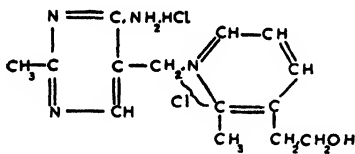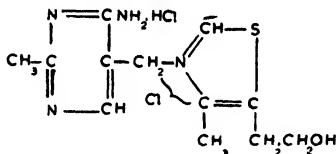
I   II

closely related to vitamin B₂ (lactoflavine) and vitamin C (ascorbic acid) has shown that alterations in the details of molecular architecture usually cause a marked diminution or complete loss of activity (*cf. e.g.* Bergel and Todd, *J.C.S.*, 1937, 1504). However, the fact that any activity at all is exhibited indicates a certain lack of specificity, and determination of the structural features necessary for vitamin activity is of importance.

Several attempts have therefore been made to effect the synthesis of (I), but so far without success. In each of

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* Since the completion of the experiments described in the present paper, successful syntheses of I have been described by Schmelkes and Joiner (*J.A.C.S.*, 1939, *61*, 2562) and Baumgarten and Dornow (*Ber.*, 1940, *73B*, 44-6).

these it was proposed as a final step to combine 2-methyl-5-bromomethyl-6-aminopyrimidine (III) with 2-methyl-3-(β-hydroxyethyl) pyridine (IV) to (I). At the time when this work was commenced experimental details for the
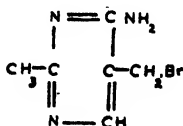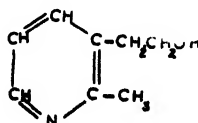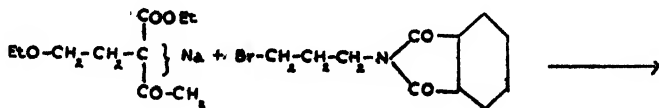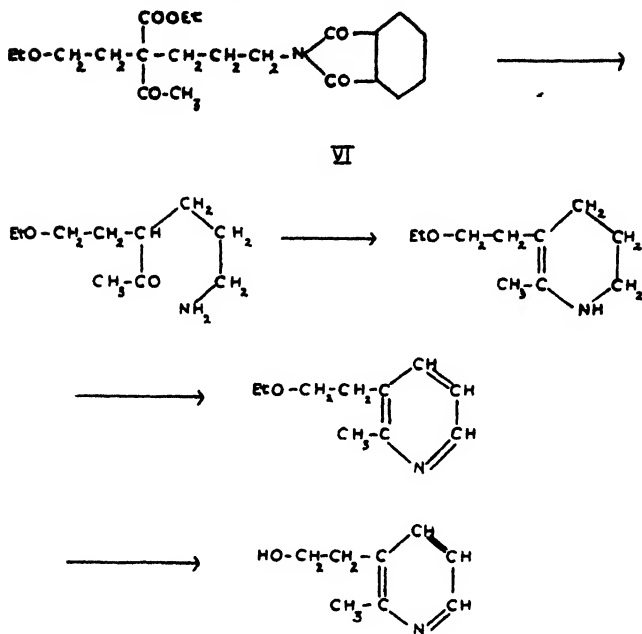
III   IV

preparation of (III) (required in the synthesis of vitamin B_1) had not been published, but the method employed had been outlined by Williams and Cline (*J.A.C.S.*, 1936, *58*, 1504). Much time was spent in endeavouring to carry out this synthesis satisfactorily, but even though, several months later, details were published by Williams, Cline and Finkelstein (*J.A.C.S.*, 1937, *59*, 1052) the yields were excessively poor. Eventually recourse was made to the method of Grewe (*Zeit. Physiol. Chem.*, 1936, *242*, 89) for the preparation of the pyrimidine portion of the molecule.

Several schemes for the preparation of IV, the pyridine half of the molecule, were investigated. The first consisted of a modification of Gabriel's synthesis of tetrahydropyridines. Gabriel (*Ber.*, 1909, *42*, 1, 1242, 1409) condensed γ-bromopropyl phthalimide with acetoacetic ester and hydrolysed the product with hydrochloric acid; on making alkaline, the resulting 1-amino-n-hexan-5-one passed spontaneously into 2-methyl tetrahydropyridine. Starting from α-acetyl-γ-ethoxy butyric ester (Clarke and Gurin, *J.A.C.S.*, 1935, *57*, 1876) it was proposed to carry out the sequence of changes shown diagrammatically below :
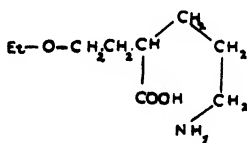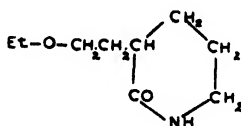
$$EtO-CH_2-CH_2-C(COOEt)(CO-CH_3)-CH_2-CH-CH_2-N(CO)_2C_6H_4$$

VI

$$EtO-CH_2-CH_2-C(CH_2)(CH_3-CO)\cdots NH_2 \longrightarrow EtO-CH_2-CH_2-C(CH_2)(CH_3-C)\cdots NH$$

$$\longrightarrow EtO-CH_2-CH_2-C(CH_3-C)\cdots N$$

$$\longrightarrow HO-CH_2-CH_2-C(CH_3-C)\cdots N$$

The sodium derivative of ethyl α-acetyl-γ-ethoxybutyrate (V) was condensed with γ-bromopropyl phthalimide in the usual manner to give ethyl α-acetyl-α-(2-ethoxyethyl)-δ-phthalimido-valerate (VI), which was obtained as a viscous oil. Attempts to eliminate the phthalic acid residue and the carbethoxyl group simultaneously were made with various hydrolysing agents ; e.g., hydrochloric acid (25% and concentrated), sodium hydroxide, sulphuric acid (50%), and hydrobromic acid (concentrated). In every case phthalic acid was split off almost quantitatively but no appreciable quantity of basic product was obtained, the small amount isolated being due to the presence of unchanged γ-bromopropyl phthalimide, which, on hydrolysis, gave rise to γ-bromopropylamine, readily identified as its aurichloride.

This disappointing failure to split off the carbethoxyl group is not unparalleled, since an examination of the literature shows that disubstituted acetoacetic esters are often extremely difficult to hydrolyse and decarboxylate. For example, after six days' boiling with dilute sulphuric acid, αα-dimethyl acetoacetic ester gives only a 25% yield of the corresponding ketone (Schryver, *J.C.S.*, 1893,

66, 1336), and α-ethyl-α-isopropyl acetoacetic ester can be purified by boiling with 10% potassium hydroxide solution, which decomposes other acetoacetic ester derivatives forming ketones (Clarke, *Amer. Chem. Journ.*, *39*, 576), Even the method of Willstätter and Hatt (*Ann.*, *418*, 151), *viz.* boiling with concentrated hydrobromic acid in glacial acetic acid, which was found so successful in the hydrolysis of α-ethyl-α-isopropyl acetoacetic ester, did not effect ketone hydrolysis of VI. It seems probable that acid rather than ketone hydrolysis occurred. It is known that the presence of large substituents in the α-position of acetoacetic esters has this influence. Support for such an assumption has been found in a paper by Lipp and Widman (*Ann.*, 1915, *409*, 130). These authors carried out a Gabriel tetrahydropyridine synthesis using ethyl α-acetyl propionate. They observed that, besides ketone hydrolysis, acid hydrolysis occurred to a large extent, the final yield of 2 : 3-dimethyl tetrahydropyridine being very small. They were able to isolate the products of acid hydrolysis, namely δ-amino-α-methyl valeric acid and its cyclic amine, 3-methyl-2-piperidone. Attempts were made to isolate some such products from the hydrolysis of VI, but although a crystalline, water soluble, compound was obtained, a satisfactory method for its purification has not yet been found. It is possibly 5-amino-2-(β-ethoxyethyl) valeric acid (VII) or its cyclic amide, 3-(β-ethoxyethyl)-2-piperidone (VIII).


The second scheme for the preparation of IV aimed at obtaining it through a corresponding quinoline derivative with the desired side chains. It is known that substitution of the benzene ring in quinoline derivatives with hydroxyl or amino groups renders it susceptible to oxidation ; and treatment with permanganate leads to formation of quinolinic acids, other side chains on the pyridine ring frequently remaining unaffected (*cf.* Besthorn and Byvanck,

Ber., 1898, *31*, 800, 802 ; Byvanck, *ibid.*, 2151). The
α-carboxyl group of the quinolinic acids thus obtained
can be removed by simple distillation, and the β-carboxyl
group by distillation with lime.

The proposed series of reactions is set out diagram-
matically below :

IX.

X.

XI

XII

IV
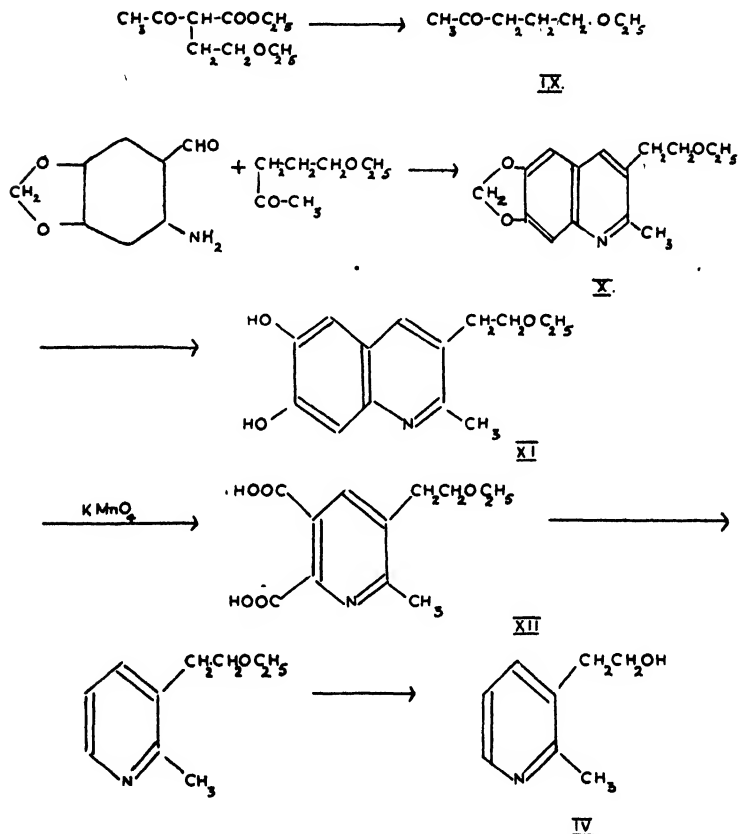
1-Ethoxy-pentan-4-one (IX) was prepared by ketone
hydrolysis of ethyl α-acetyl-γ-ethoxy butyrate, and was
condensed with 6-aminopiperonal to give 2-methyl-3-
(β-ethoxyethyl)-5 : 6-methylenedioxyquinoline (X) in good
yield (Friedländer's synthesis ; *cf., e.g.* Robinson, *J.C.S.*,
1922, *121*, 832). There can be little doubt that the longer
β-ethoxyethyl side chain goes into the 3-position of the
resulting quinoline derivative, since there are many
analogous reactions.

This compound (X) proved peculiarly resistant to demethylenation by the phoroglucinol-sulphuric acid method used by Späth and Quietensky (*Ber.*, 1927, *60*, 1882, 1891) for the demethylenation of certain alkaloids. An attempt was therefore made to demethylenate by heating under pressure with methyl alcoholic potassium hydroxide, a method employed by Späth and Lang (*Ber.*, 1921, *64*, 3064) for hydrolysis of the methylenedioxy group under conditions leaving methoxyl groups intact. The advantage of the method lies in the rapid destruction of the formaldehyde produced, the disadvantage in the decomposition phenomena which may occur with the use of alkali at high temperatures.

No phenolic substances could be isolated from the reaction mixture, although an ethereal extract of the neutralised mixture gave a red colour with ferric chloride. An attempt was therefore made to effect oxidation of the intermediate catechol derivative (XI) without preliminary isolation, and then to precipitate the resulting pyridine dicarboxylic acid (XII) as its copper salt. A few grams of a copper salt were obtained. However, on endeavouring to decarboxylate by distillation with lime, only a small amount of basic distillate was obtained. This could not be characterised.

A third scheme proposed for the preparation of IV was very similar to the first, except that acetylacetone was substituted for acetoacetic ester. The advantages of using acetylacetone in place of acetoacetic ester are (1) that, being symmetrical, hydrolysis can only take place in one way, by removal of one of the acetyl groups; whereas with acetoacetic ester the acetyl group is removed in preference to the carbethoxyl group when the substituents are large; and (2) that the larger the substituents in acetylacetone, the more readily is it hydrolysed by acids (*cf.* Adkins, Kutz and Coffman, *J.A.C.S.*, 1930, *52*, 3212-21). In substituted acetoacetic esters, on the other hand, the presence of two α substituents makes hydrolysis of the carbethoxyl group very difficult, and impossible when the groups are large.

The ease of hydrolysis of substituted acetyl acetones is so great that they cannot be prepared in the usual way by condensation with alkyl halides in the presence of sodium ethoxide solution. Instead the dry sodium salt must be prepared by treating the diketone with finely divided sodium in ether, and this combined with the alkyl halide

by heating with it alone or in an appropriate solvent (*cf.* Auwers and Jacobson, *Ann.*, 1922, *426*, 161–236 ; Morgan and others, *J.C.S.*, 1924, *125*, 754, 760 ; 1926, *127*, 797–806, 2611–25). Usually the yields are poor and it is difficult to introduce a second substituent.

Sodio-acetylacetone was condensed with β-ethoxyethyl bromide to give β-ethoxyethyl acetylacetone in 27% yield, but investigation of the condensation of the latter with γ-bromopropyl phthalimide, or of γ-bromopropyl phthalimide with acetylacetone itself had not been undertaken when the work was abandoned.

Experimental.

Ethyl α-acetyl-γ-ethoxybutyrate (*V*).

This ester was prepared according to the method of Clarke and Gurin (*J.A.C.S.*, 1935, *57*, 1876). The product on distillation *in vacuo* boiled continuously from 70° to 113° at 10–12 mm. Fractionation through a Golodetz column gave, after removal of the lower boiling products, a colourless oil (127 g., *i.e.* 32%) boiling constantly at 125°/12–13 mm. Since Clarke and Gurin record a boiling point of 85–90° at 10 mm., it was considered advisable to examine the properties of the product. It was found to be insoluble in water and sodium carbonate solution, even on boiling, but was soluble in hot sodium hydroxide solution ; it gave a blue colour with ferric chloride (enol grouping) and reacted with metallic sodium (active hydrogen). No solid derivatives such as a semicarbazone or pyrazolone could be obtained, but an analysis confirmed the identity of the product.

Found : C=59·5, H=8·9% ; calculated for C$_{10}$H$_{18}$O$_4$: C=59·4, H=8·9%.

The boiling point of the product at 1·5 mm. was 95–97°. It therefore seems probable that the boiling point recorded by Clarke and Gurin (85–90°/10 mm.) is that at 1 mm.

Ethyl α-acetyl-α-(2-ethoxyethyl)-δ-phthalimido valerate (*VI*).

Ethyl α-acetyl-γ-ethoxybutyrate (20·2 g.) and γ-bromo-propylphthalimide (26·8 g.) were added successively to a solution of sodium (2·5 g.) in absolute alcohol (70 c.c.). The mixture was then refluxed for seven hours, sodium bromide being precipitated. After neutralisation with hydrochloric acid, alcohol and unchanged ester were removed by steam distillation. The oily residue which

remained was taken up, washed with water, and dried in ether. · The ether was then removed under diminished pressure, leaving a viscous oil (18·4 g., *i.e.* 47%). A sample of the oil was distilled *in vacuo* and came over at 230–235°/5 mm. After standing for several weeks unchanged γ-bromopropyl phthalimide crystallised out. This was removed by filtration and the filtrate, a pale yellow oil, analysed.

Found : C=64·4, H=6·8% ; calculated for $C_{24}H_{28}O_6N$: C=64·8, H=6·9%.

1-Ethoxy-pentan-4-one (IX).

Several methods for the ketone hydrolysis of the ester (V) to the ketone (IX) were examined, typical experiments being as follows :

(a) With 2·5% sodium hydroxide solution.

The ester V (115 g.) was mixed with alcohol (100 c.c.) and 2·5% sodium hydroxide solution (1,500 c.c.) and allowed to stand for twenty-four hours at 0°. The solution was then acidified with hydrochloric acid and heated on the water bath until evolution of carbon dioxide ceased (the solution was finally boiled). It was then fractionated to remove alcohol before extraction with ether. The fraction 78–96° was collected and the remainder continuously extracted with ether. Since the aqueous alcoholic distillate smelt strongly of an ester or ketone, it was refractionated to remove alcohol and the residue extracted with ether. The combined ethereal extracts were dried over anhydrous sodium sulphate and the ether removed. The residue distilled as a colourless oil (48 g.) at 172–174° at atmospheric pressure. It gave a dinitrophenyl-hydrazone which on recrystallisation from aqueous alcohol was obtained in orange crystals melting at 55°.

Found : N=18·2% ; calculated for $C_{13}H_{15}O_5N_4$: N= 18·1%.

· The poor yield may be ascribed to a certain amount of acid hydrolysis or to the volatility of the ketone in alcohol and water vapour.

(b) With water under pressure (cf. Meerwein, *Ann.*, 1913, *398*, 242).

Ethyl α-acetyl-γ-ethoxybutyrate (20 g.) and water (50 c.c.) were heated in an autoclave at 250° for half an

hour. The solution then gave no colour with ferric chloride. The extent to which acid hydrolysis had occurred was determined by titration with N/10 sodium hydroxide solution. 135 ml. of N/10 sodium hydroxide were required for neutralisation ; therefore acid hydrolysis had occurred to the extent of 7%.

The solution was extracted with ether, and ethereal extract dried over anhydrous sodium sulphate and the ether removed. The ketone (6·5 g.) distilled at 172–174° at atmospheric pressure.

2 - Methyl- 3 -(β-ethoxyethyl) -5 : 6 -methylenedioxy-quinoline (X).

6-Aminopiperonal (31 g.) and 1-ethoxypentan-4-one (27 g.) were dissolved in ethyl alcohol (200 ml.). Potassium hydroxide solution (200 ml. of 33%) was added and the mixture refluxed on the water bath for two hours. After distillation of portion of the alcohol, addition of water to the residue caused a flocculent white precipitate to come down. This was filtered off and dried (yield 42 g.). After recrystallisation from petroleum ether (60–80°), beautiful pale yellow needles melting at 83° were obtained.

Found : C=69·0, H=6·6, N=5·5% ; calculated for $C_{15}H_{17}O_3N$: C=69·5, H=6·6, N=5·4%.

The *picrate*, precipitated from alcohol solution and recrystallised from the same solvent, formed yellow needles, m.p. 216°.

Found : N=11·6% ; calculated for $C_{21}H_{20}O_{10}N_4$: N= 11·5%.

The *methiodide* was obtained by heating with an excess of methyl iodide in a corked tube on the water-bath for fifteen minutes. Recrystallised from alcohol it formed pale yellow needles melting at 196°.

Found : N=3·5% ; calculated for $C_{16}H_{20}O_3NI$, N= 3·5%.

Condensation of Acetylacetone with β-Ethoxyethyl Bromide.

Dry sodio-acetylacetone was prepared according to the method of Morgan and Rawson (*Chemistry and Industry*, *44* (Pt. 2), 462T). Sodio-acetylacetone (20 g.) was refluxed with β-ethoxyethyl bromide (100 g., 4 mols.) with addition of sodium iodide (2 g.) for twenty-four hours in an oil bath maintained at 180–200°. The mixture was filtered and the precipitated sodium bromide washed with ether. The

filtrate and washings were combined, the ether and excess ethoxyethyl bromide distilled off under ordinary pressure, and the residue distilled under reduced pressure.   A yellow oil (5·8 g.) was obtained boiling at 110–120° (mainly 114–115°) at 23·5 mm.   This corresponds to a yield of 21%. The product gave a brownish red colour with ferric chloride and a copper salt with copper acetate solution.   The latter was recrystallised from ethyl alcohol, giving soft light grey needles, m.p. 183°.   The oil was analysed.

Found : C=62·2, H=9·1% ; calculated for $C_9H_{16}O_3$, C=62·8, H=9·3%.

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THE ISOMERISM OF DIAZOAMINOAZO COMPOUNDS.

By F. P. DWYER, M.Sc.

In a previous paper (THIS JOURNAL, 1940, *74*, 99) the suggestion was made that the development of intense colours when diazoaminoazo compounds are dissolved in alcoholic alkali, or adsorbed, on magnesium or cadmium hydroxides was due to a tautomeric change in the molecule to yield a quinoid form. In pursuance of this suggestion it was observed that whilst there was a considerable variation in the colours of the diazoaminoazo compounds themselves, the N-methyl derivatives were all orange yellow. It will be appreciated that in both the diazoaminoazo compounds and their N-methyl derivatives, two chromophores are operative—the triazene group –N=N–NH–, and the azo group –N=N– ; but in the unmethylated compounds there is also the possibility of tautomeric change to yield the strong quinoid chromophore. It follows, therefore, that where the diazoaminoazo compound is very much more strongly coloured than its N-methyl derivative, this latter chromophore is probably present.

If the nitrodiazoaminoazo compounds are excluded (since there is a possibility of tautomeric migration of the hydrogen to the nitro group), it is found that diazoaminoazobenzene itself, and 3-methylbenzenediazoaminoazobenzene are dark red, but yield orange yellow N-methyl derivatives, and probably exist normally in the quinoid form. On the other hand, 2-methyl and 4-methylbenzenediazoaminoazobenzene are orange yellow to brown, yield N-methyl derivatives of the same colour, and probably exist in the triazene (true diazoaminoazo) form.

In this paper the preparation of the missing triazene form of diazoaminoazobenzene, and both forms of the silver salt are described ; but on account of its instability and difficulties in its preparation no success has attended

efforts to prepare the triazene form of 3-methylbenzcne-diazoaminoazobenzene.

<div align="center">EXPERIMENTAL.</div>

Diazoaminoazobenzene—Quinoid Form.

This substance prepared by the original method of Nietzki and Diesterweg (*Ber.*, 1888, *21*, 2143) with the modification that the diazotised p-aminoazobenzene was first neutralised with sodium carbonate before coupling with aniline, gave bright purplish red leaflets and prisms, M.P. 121–122°. In several instances by crystallisation from acetone in the presence of ammonia, the substance crystallised in the form of thick rounded nodules of a distinct purplish violet colour. This difference was apparently only due to grain size since the melting point was the same, and the finely powdered substance was red. The same substance in brilliant red plates and leaflets was obtained from carbon tetrachloride. If the substance was dissolved in cold acetone, and immediately poured into water, it crystallised unchanged, M.P. 120–121°. Nietzki and Diesterweg (*loc. cit.*) give M.P. 118–119°, and Earl (THIS JOURNAL, 1930, *64*, 96), 119·5°.

Found : $N = 23·33\%$; calculated for $C_{18}H_{15}N_5$, $N = 23·26\%$.

Triazene Form.

The quinoid form was easily soluble in pyridine to a deep red solution, and if petroleum ether was added to the saturated solution a dark red oil resulted. Left in contact with petroleum ether for 2–3 days the oil solidified to a mass of brownish yellow needles of the triazene form. The same substance could be obtained in very small amounts by dissolving the quinoid form in alcohol and then adding a strong solution of caustic alkali when it was precipitated. The best yields were obtained by allowing a saturated solution of the quinoid form in amyl acetate to evaporate slowly in an open dish. In about an hour a slight precipitate commenced to come down, and when the whole of the solvent had evaporated the transformation had proceeded to the extent of about 70%. The unchanged quinoid form could be extracted with hot petroleum ether.

In order to eliminate the possibility that this form is due to cis/trans isomerism about the doubly bonded

nitrogen atom (Hartley, *J. Chem. Soc.*, 1938, 633) a saturated solution of the quinoid form in amyl acetate was exposed to ultra-violet light from a mercury lamp for four hours.   No colour change occurred, and no precipitate came down.

The pure triazene form crystallised in yellowish brown microscopic needles, M.P. 138–139°.   A mixture of the quinoid and triazene forms in approximately equal parts melted at 142–143° with softening at 138°.   This peculiar elevation of the melting point may be ascribed to salt formation between the feebly basic triazene form and the distinctly acidic quinoid form, and has also been observed with the normal and acid forms of 4 : 4′ dinitrodiazoaminobenzene (F. P. Dwyer, *J. Soc. Chem. Ind.*, 1938, *57*, 351). The triazene dissolved only very slowly in petroleum ether, benzene, and amyl acetate in the cold, transformation into the quinoid form occurring at the same time.   However, if dissolved in cold acetone, in which it gave an orange solution, and immediately poured into cold water, a precipitate resulted, which under the microscope was found to consist mostly of needles of the triazene form and a few crystals of the quinoid form.   The precipitated substance melted at 139–140°.

Found :   N = 23·46% ;   calculated for $C_{18}H_{15}N_5$,   N = 23·26%.

Silver Salt of the Triazene Form.

Diazoaminoazobenzene (either form) (1·35 g.) was dissolved in 50 mls. of methanol containing 2·0 gms. of anhydrous sodium acetate.   To this solution was added a solution of silver nitrate (0·98 g.) dissolved in hot methanol (50 mls.), pyridine (5 mls.), and sodium acetate (2 g.). The resulting orange yellow precipitate was washed with methanol and then water, and dried at room temperature. The dry powder was then dissolved in a slight deficiency of pyridine at 85°.   The deep orange-red solution was filtered rapidly and allowed to cool to 25°, and the silver salt of the triazene form filtered off.   After washing with acetone, it was dried at room temperature in a desiccator over concentrated sulphuric acid.   The substance crystallised in minute orange yellow needles, which decomposed with incipient melting at 200–205°.   It was dissolved only very slowly by cold pyridine to an orange yellow solution, which darkened to red on warming slightly.   This behaviour was most distinctive.   The substance was very sparingly

soluble in hot acetone, and slightly soluble in warm nitrobenzene. It contained no coordinated pyridine.

Found: Ag=26·33%; calculated for $C_{18}H_{14}N_5.Ag$, Ag=26·53%.

Silver Salt of the Quinoid Form.

The orange yellow salt of the triazene form was dissolved in a slight deficiency of pyridine at 85° as before and cooled rapidly to 20°. After filtration, the orange red solution was cooled in a freezing bath to −10°. The colour darkened very considerably, but no precipitate came down. Three times the volume of methanol cooled previously to −10° was then added slowly over 10 minutes, stirring continuously, and maintaining the temperature at −10°. A bright scarlet powder was deposited. It was removed by rapid filtration, washed with cold methanol, and dried at room temperature over concentrated sulphuric acid. Under the microscope the scarlet powder consisted of minute clusters of leaflets. It melted at 195–200°, and exploded at 205°. No observable colour change occurred on heating. The substance was extremely soluble in cold pyridine to a dark red solution ; but only sparingly soluble in warm nitrobenzene. Attempts to prepare a pyridine coordination derivative failed.

Found: Ag=26·31%; calculated for $C_{18}H_{14}N_5.Ag$, Ag=26·53%.

Methylation Experiments.

The silver salt of the triazene form was refluxed with methyl iodide and acetone. After reaction was complete, the silver iodide was filtered off, and the orange yellow solution precipitated with water. After several crystallisations from aqueous alcohol, the orange yellow flakes of the N-methyl derivative melted at 84–85°. The same substance was obtained from diazoaminoazobenzene and methyl iodide in the presence of caustic potash (Dwyer, This Journal, loc. cit.).

Attempts to prepare the methyl derivative of the quinoid form proved fruitless. When the silver salt of the quinoid form was refluxed with methyl iodide in acetone solution it gave the above N-methyl derivative, M.P. 84–85°. At −5° or at room temperature a mixture of the silver salt of the quinoid form with methyl iodide in benzene solution gave no reaction even after a month.

Molecular Weight Determinations.

The molecular weight of the quinoid form of diazoaminoazobenzene was determined in benzene cryoscopically. A slight association was noted, and may be ascribed to a slight transformation to the triazene form followed by salt formation. At the end of the determination the benzene solution was allowed to evaporate and the melting point of the residue determined. It melted at 119–120° ; but under the microscope a few crystals of the triazene form could be detected.

Found : M=351, 360 ; calculated for $C_{18}H_{15}N_5$, mol. wt. =301.

Attempts to determine the molecular weight of the triazene form were unsuccessful. Tests showed that owing to the slow rate of solution of the substance in cold benzene, the transformation to the quinoid form was almost complete before a sufficient concentration could be obtained.

In the case of the silver salts, although the molecular weights could be determined in pyridine (Rast, *Ber.*, 1921, *54*, 1979), it was evident that an equilibrium was rapidly attained in solution, and any results would be quite unreliable.

DISCUSSION.

The two forms of diazoaminoazobenzene and of the silver salts described in this paper may be either isomeric, dimorphous, or polymeric. A method of testing for dimorphism discussed by Mellor (THIS JOURNAL, 1937-38, *71*, 536) consists in observing solutions of both forms in the same solvent, when if they are dimorphous, the solutions should be identical. The fact that both forms of diazoaminoazobenzene can be dissolved in cold acetone and then recovered under identical conditions, indicates that in this solution both forms retain their identity, and hence cannot be dimorphous. In the case of the two silver salts, the colours of the pyridine solutions are quite distinct, and dimorphism must be ruled out.

The possibility of polymerism is usually eliminated by molecular weight determinations, but since this test could not be applied to the orange-yellow form of diazoaminoazobenzene, it is possible that this form is a polymer of the purplish red form. However, molecular weight determinations on a wide variety of diazoamino compounds, which contain the same triazene grouping

-N-N-NH-, show that the association of diazoamino compounds is very slight, and only just noticeable in very concentrated solutions (Hunter, *J. Chem. Soc.*, 1937, 320). This opinion is also confirmed by dipole measurements (Le Fevre, *ibid.*, 1937, 1805). Further, all experience indicates that the more stable form is always the associated form, in which event the purplish red form should be associated. For these reasons, and in view of the marked differences in colour, it is considered that these substances are isomeric.

In view of its colour the orange yellow form is considered to be the true diazoaminoazo compound of constitution I ; and the purplish red form the quinoid isomer II.

$$C_6H_5.N=N-NH.C_6H_4.N=N.C_6H_5$$
$$\text{(I)}$$
$$C_6H_5.N=N-N=C_6H_4=N-NH.C_6H_5$$
$$\text{(II)}$$
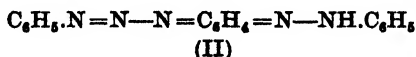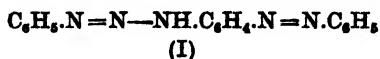
The two silver salts which crystallise from pyridine without any of the solvent being coordinated must be considered as internally coordinated complexes. In agreement with the constitutions found for the silver salts of diazoaminobenzene, and 4 : 4' dimethyldiazoaminobenzene, the orange yellow silver salt of the true diazoaminoazo compound I has the constitution III.

$$C_6H_5.N-N=N.C_6H_4.N=N.C_6H_5$$
$$\diagdown\diagup$$
$$Ag$$
$$\text{(III)}$$
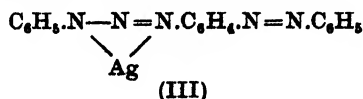
The scarlet silver salt of the quinoid form II must be formulated as a dimeric complex IV. Any other formulation must admit of a para chelate bridge, which is unlikely on steric grounds, or leave the silver coordinately unsaturated, in which event it should have coordinated with pyridine.

$$C_6H_5.N=N-N=C_6H_4=N-C.C_6H_5$$
$$|\qquad\qquad|$$
$$Ag\qquad\qquad Ag$$
$$C_6H_5.N-N=C_6H_4=N-N=N.C_6H_5$$
$$\text{(IV)}$$
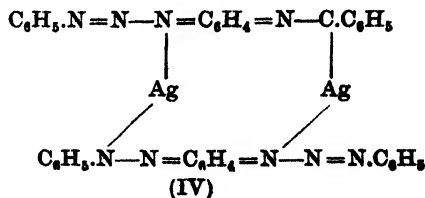
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THE CORALS OF THE GARRA BEDS, MOLONG DISTRICT, NEW SOUTH WALES.

By DOROTHY HILL, M.Sc., Ph.D.,
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(Communicated by DR. IDA A. BROWN.)

With Plates II-VIII.

INTRODUCTION.

The species of corals described in this paper are, except for *Favosites nitidus* from Victoria, from localities within the Garra Beds of the Molong district of New South Wales, described by Joplin and Culey (1938). The beds consist of limestones, calcareous shales, tuffs, and quartzites, and contain a coral-brachiopod fauna; they succeed the Silurian Manildra Beds of tuffs, cherts, and indurated shales, and are overlain by conglomerates and reddish, coarse grits, sandstones, and shales referred to the Upper Devonian Lambie Stage. Etheridge[1] referred two species from localities within the Garra Beds to the Upper Silurian (1907, p. 41); Joplin and Culey (1938) have considered the Garra Beds to be Middle Devonian. Specimens from Curra Ck. near Wellington are included, as they are from beds which Joplin and Culey (*in litteris*) consider are probably a northern continuation of the Garra Beds.

The following species are described from the Garra Beds :

MADREPORARIA RUGOSA.

Family ACANTHOPHYLLIDÆ.

Family CALCEOLIDÆ.

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[1] Throughout this paper " Etheridge " refers to R. Etheridge, Junr.

Age. (*a*) The Rugosa. *Acanthophyllum* sp. has close
resemblances to species from the Lower Devonian of the
Carnic Alps, and the beds transitional between the Lower
and Middle Devonian in France. *Spongophylloides* (?)
thomasæ is only doubtfully referred to this Silurian genus.
Rhizophyllum ranges through the Gotlandian and Lower
Devonian, but is not known in the Middle Devonian.
Cystimorphs are characteristic of both Silurian and
Devonian. *Pseudamplexus* occurs in the Upper Silurian
and the Lower and Middle Devonian. *Tryplasma* ranges
from the Upper Ordovician or Lower Silurian into the

Lower Devonian. *Entelophyllum* is known elsewhere only from the Silurian. The occurrence of *Rhizophyllum* and *Tryplasma* thus suggests that the beds are nòt later than Lower Devonian, and *Entelophyllum* strengthens this view. *Acanthophyllum* sp. indicates a Lower Devonian rather than an Upper Silurian age, and *Pseudamplexus* does not refute this. The Rugosa thus suggest a Lower Devonian age.

(*b*) The Tabulata. These are a mixture of species which occur elsewhere in the Silurian, the Lower Devonian or the Middle Devonian. Thus *Favosites gothlandicus* is Silurian, being represented also in beds transitional between the Lower and Middle Devonian in France, and in the Lower and Middle Devonian elsewhere in Europe by forms closely related to its three Silurian formæ. *F. ovatiporus* occurs in the Lower Devonian of Loyola ; *F. bryani* and *F. goldfussi* are known elsewhere in the Lower Middle Devonian, *F. goldfussi* extending into the Upper Middle Devonian. *Striatopora* sp. and *Syringopora* sp. are of no assistance in determining the age. This mixture of *Favosites* is thought to indicate a Lower Devonian age.

(c) The Heliolitida. *Heliolites daintreei* is a Silurian and Lower Devonian species, and *Plasmopora gippslandica* occurs in Silurian and Middle Devonian beds elsewhere in Australia, so that the Heliolitida indicate a broad Siluro-Devonian period.

Considering all three groups of the Madreporaria, a Lower Devonian age seems most likely for the Garra beds. One genus and a species contained in them are Silurian only elsewhere, as well as some forms that are otherwise Lower and Middle Devonian. These two limits indicate a horizon somewhere between them in the Lower Devonian, and this is supported by the occurrence of the Lower Devonian *F. ovatiporus*, and of *Acanthophyllum* sp. with Lower Devonian affinities. Direct comparison with Lower Devonian faunas is difficult as the calcareous facies was not widely developed in beds of that age. *Favosites goldfussi*, *F. gothlandicus* and *Heliolites daintreei* are species occurring also in Europe.

In comparing the coral fauna of the Garra beds with that of the Lower Couvinian Bluff limestone of the Murrumbidgee R., which is the lowest known Middle Devonian fauna in Australia, we find only the genera *Acanthophyllum*, " *Cystiphyllum* " and *Favosites* in common ; a wider

comparison with the whole Couvinian succession of the Goodradigbee R., adds to these only the genus *Pseudamplexus*. The only identical species is *Favosites bryani*, which occurs in the Garra beds and in the Murrumbidgee R. Couvinian, but the Garra specimens are atypical. A comparison with the Lower Devonian of Loyola shows the first three genera above common to both, but the distinctive *F. ovatiporus* suggests similarity of age. With the Silurian fauna of Yass there are seven genera in common, *Rhizophyllum*, " *Cystiphyllum*," *Tryplasma*, *Entelophyllum*, *Favosites*, *Heliolites* and possibly *Plasmopora*, and at least two species, *F. gothlandicus* and *H. daintreei*, are identical. But *H. daintreei* ranges as high as the Middle Devonian, and it is suggested later in this paper that *F. gothlandicus* occurs as high as the transitional horizon between the Lower and Middle Devonian in France. Although the Garra fauna does not compare closely with any other known assemblage, we think it nearest in age to that of the Lower Devonian of Loyola, as with it there is the only definite identity of a short-range species.

MADREPORARIA RUGOSA.

Family ACANTHOPHYLLIDÆ.

Acanthophyllidæ, Hill, 1939a, p. 56 ; 1939b, p. 220.

Rugosa with a wide dissepimentarium of highly arched dissepiments, long septa frequently modified in the dissepimentarium and carinate in the tabularium, and with numerous, shallowly concave tabulæ deepened at the axis. The major septa are long and unequal, never amplexoid, and the two minor septa neighbouring the counter septum are longer than the rest.

The diagnosis of the family is widened to include the Silurian genera *Spongophylloides* Meyer (see Butler, 1934) and *Cymatelasma* Hill and Butler (1936), and the Lower Devonian genus *Lyrielasma* Hill (1939b, p. 243), all of which have the family characters of numerous, shallowly concave tabulæ, deepening at the axis, long unequal major septa, carinate in the tabularium, never amplexoid, and except in *Lyrielasma*, two very long minor septa flanking the counter septum. Formerly (1939b, p. 243) I considered *Spongophylloides* and *Cymatelasma* as the family Cymatelasmidæ, and thought that the resemblance to them of *Lyrielasma* was not close enough to unite all three in the one family. But the chief difference between these three

genera and those I formerly included in the Acanthophyllidæ was in the characters of the septa in the dissepimentarium, and it now appears to me that such variability is as much diagnostic of the family Acanthophyllidæ as the fixity in the characters of the tabularium. The range of the family is thus extended down into the Gotlandian.

Range. Gotlandian of Europe, Lower and Middle Devonian of Europe and Australia, and Upper Devonian of Europe.

Genus Acanthophyllum Dybowski.

Acanthophyllum Dybowski, 1873, p. 339 ; 1874, p. 493.
Acanthophyllum Hill, 1939a, p. 56 ; 1939b, p. 222.

Genolectotype : Cyathophyllum heterophyllum Edwards and Haime, 1851, pl. x, figs. 1a-c. Devonian, Eifel.

Diagnosis. Rugosa with a wide dissepimentarium of small, highly arched dissepiments, with shallowly concave, axially deepened tabulæ, and with long, but unequal major septa. The axial ends of the major septa are arranged in groups in the tabularium, and are straight, or curved vortically, the curvature differing in degree from group to group ; the cardinal septum is typically short, and one septum, not a protoseptum, extends to the axis. The septa show different types of modification ; they are frequently much dilated, either in the dissepimentarium or more rarely in the tabularium, or in both ; towards the periphery they may be thin and lined with lateral dissepiments ; in the tabularium they are typically waved and carinate.

Range. Probably *Actinocystis perfecta* Wedekind (1927, p. 45, pl. xxvi, figs. 15–18), from the Ludlovian of Gotland, is a member of the genus, and if so the range of the genus, formerly given as Lower and Middle Devonian of Australia and Europe, and Upper Devonian of Europe, must be extended down into the Upper Silurian.

Acanthophyllum sp.
(Plate II, figs. 1, 2.)

Holotype. 5171, Sydney University Collection, Garra Beds, Por. 81, Par. Brymedura, Molong District, N.S.W.

Diagnosis. Slenderly trochoid or cylindrical *Acanthophyllum* with narrow dissepimentarium, and septa more dilated in the dissepimentarium than in the tabularium.

Description. The corallum is solitary, and elongately trochoid or cylindrical; one specimen has a diameter of 9 mm., and another, the holotype, of 15 mm. The epitheca of the holotype appears smooth. The 22 to 25 major septa are unequal, the longest extending to the axis, the others almost to the axis. In the holotype the longest septum appears to be the cardinal, while in the second specimen the counter septum seems the longest. The other major septa are arranged in groups as is typical in *Acantho-phyllum.* In the holotype they are slightly curved, particularly at their axial ends, but in the second specimen they are almost straight. They are more carinate in the holotype, and are considerably dilated in both dissepimentarium and tabularium in both specimens, particularly at the periphery of the second, where a peripheral stereozone is formed. The tabulæ are flat or slightly sagging, incomplete, and closely spaced; the dissepiments in the second specimen are very large, in not more than two series, sometimes dilated.

Remarks. In its internal structure this species shows considerable resemblance to that of the Lower Devonian fasciculate genus *Lyrielasma,* particularly in the tendency of either the counter or the cardinal septum to be the longest, and in the type of septal dilatation in the dissepimentarium. Very close resemblances are also seen to *Cyathophyllum dianthus* Goldfuss, Le Maitre (1934, p. 153, pl. v, fig. 13) from the Chaudefonds limestone, representing the base of the Middle Devonian and the top of the Lower Devonian, and *C. dianthus* of Charlesworth (1914, p. 363, pl. xxxi, fig. 8) from the Lower Devonian of the Carnic Alps.

Localities. Por. 81, Parish Brymedura, Molong District, N.S.W. (Sydney University Collection, 5171); 10 miles north of Molong on the Cumnock Road (probably Por. 52, Parish Eurimbula) (F.3491, University of Queensland Collection). Both Garra Beds.

Genus Spongophylloides Meyer.

Spongophylloides Meyer, 1881, p. 109.

Spongophylloides Lang and Smith, 1927, p. 459; Butler, 1934, p. 541.

Genotype. Spongophylloides schumanni Meyer, 1881, p. 109, pl. v, fig. 12. Drift. East Prussia = (see Lang and Smith, 1927, p. 459) *Cystiphyllum grayi* Edwards and Haime, 1851, p. 465.

Diagnosis. Rugose corals, typically solitary, with major septa which reach or nearly reach the axis, and with a peripheral zone of lonsdaleoid dissepiments in which the septa are developed only as crests, the minor septa being confined to the inner part of the dissepimentarium where normal dissepiments are developed. The septa are wavy, and may be more or less dilated. The tabular floors are concave, deepened axially, and the tabellæ are small, close and but slightly arched.

Remarks. The arrangement of the axial ends of the septa in *Spongophylloides* is very similar to that in *Acanthophyllum*, but the longest septum is not invariably a metaseptum. The peripheral zone of lonsdaleoid dissepiments, which is very well developed in *Spongophylloides*, serves thereby to distinguish this genus.

Spongophylloides (?) thomasæ sp. nov.

(Plate IV, figs. 1*a*, 1*b*.)

Holotype. NS 1296, Sydney University Collection, Garra Beds, near Cudal, N.S.W. This is the only specimen known. Collector, Miss N. Thomas.

Diagnosis. Cerioid *Spongophylloides* with very large corallites, very numerous long major and minor septa, and some geniculate dissepiments.

Description. The corallum is cerioid, the holotype consisting of parts of three adult corallites and an intermural offset. The diameter of the largest corallite is at least 40 mm. The offset has a diameter of 5 mm., and a wide peripheral zone of lonsdaleoid dissepiments. The largest corallite has a peripheral zone 10 mm. wide of large lonsdaleoid dissepiments, in which the septa are represented only by crests on the dissepiments. Attenuate major and minor septa, 33 of each, are both well developed inside this zone ; the parts of the minor septa inside this zone are a little over 10 mm. long, while the major septa are unequal, extending to or almost to the axis ; they are slightly wavy and weakly carinate, both waves and carinæ being parallel to the distal edges of the septa. The tabulæ are closely spaced and incomplete, forming concave floors to the tabularium, with a deep axial depression. The lonsdaleoid dissepiments in the peripheral zone are large, elongate plates, horizontally based, or inclined at about 45°. The inner series of dissepiments are of smaller and

more globose plates, more steeply inclined, and frequently geniculate in transverse section.

Remarks. The known species of *Spongophylloides* are solitary, occurring in the Silurian. This cerioid form is placed somewhat doubtfully in the genus. The general arrangement of its septa is like that of the Acanthophyllidæ, even more like that in *Acanthophyllum* than that in *S. grayi*, but it may be that the resemblance in internal structure to *Spongophylloides* is homœomorphic.

Family CALCEOLIDÆ.

Calceolidæ Lindström, 1883, p. 9 ; Hill, 1940.

Genus Rhizophyllum Lindström.

Rhizophyllum Lindström, 1866a, p. 279 ; 1866b, p. 411 ; 1883, p. 22.

Rhizophyllum Hill, 1940b, *q.v.* for Australian Silurian species.

Genotype. *Calceola gotlandica* Roemer, Upper Silurian, Gotland.

Diagnosis. Calceoloid corals with semi-circular operculum ; with undilated, arched, horizontal skeletal elements, none of which extend completely across the lumen, and with vertical skeletal elements reduced to a series of short septa, partly lamellar and partly acanthine, on the flattened side of the corallum.

Range. Gotlandian of Europe, North America and Australia, and Lower Devonian of France.

Rhizophyllum enorme Etheridge.
(Plate II, figs. 3, 4.)

Rhizophyllum enorme Etheridge, 1903, p. 232, pl. xlvii, Boree Ck., Portion 3, Parish of Cudal, Co. Ashburnham, near Molong, N.S.W.

Type Material. Unlocated, formerly in the collection of the Geological Survey of New South Wales.

Diagnosis. Very large, sub-erect *Rhizophyllum*, up to 130 mm. in length.

Description. The corallum is large, the largest specimen collected being incomplete at 120 mm., and the smallest 45 mm. long. There is a slight curvature of the whole corallum, so that the flat (counter) side rests with the calical and apical portions inclined upwards. This

curvature is greatest near the apex. Increase in diameter is rapid at first, 40 mm. being attained in a height of 25 mm. ; thereafter it is slow. In transverse section the corallum is semi-circular in the earlier stages, but becomes more flattened with height, the length of the flattened side between the alar septa being more than twice the width between the cardinal and counter sides. The angles at the alar septa are rounded, so that the greatest width of the corallum is a little to the cardinal side of the alar septa. The epitheca shows marked interseptal ridges and interseptal furrows, and transverse striæ ; growth constrictions also occur. A broad ridge is seen external to the counter septum. The calical characters are imperfectly known ; the cardinal side is set slightly below the flattened side, and there is a deep pit near the inner end of the cardinal septum : there is a row of alternating major and minor septa along the flattened border of the calice, except at the angles, but none have been observed along the curved border. Fairly large domed plates are visible. The operculum is not known in association with any specimen.

The lumen is filled with unthickened rather large domed horizontal skeletal elements, inclined downwards to a deep fossula at the alar and counter septa. The major septa may extend half-way across the lumen from the flattened edge ; none are seen in the cardinal quadrants ; they are longest at the middle line, and shorten gradually towards the angles. They are straight, alternating in size, and each consists of large, distant trabeculæ so thickened as to be in contact.

Remarks. The species differs from all others by its great size, transcending even *R. gervillei* (Bayle) from the Lower Devonian of France. In proportions and internal structure it is closest to the Gotlandian *R. gotlandicum*, and the Australian Silurian *R. robustum* Shearsby. It occurs in Mandagery's Ck., Por. 73 or 77, Par. Brymedura in addition to the type locality.

CYSTIMORPHS.

This morphological group, which is probably polyphyletic, has already been reviewed (Hill, 1939*b*, p. 248).

"Cystiphyllum" sp.

(Plate II, figs. 5, 6.)

Cylindrical cystimorphs, with average diameter 20 mm., are common in the Garra Beds, at all localities where

corals were collected. Many individuals occur together, possibly forming fasciculate colonies, but this was not proved, no evidence of branching being seen. Fragments 130 mm. long were obtained. The epitheca shows growth striæ, and many growth swellings and constrictions, and with slight weathering longitudinal furrows corresponding to the septa are visible. No vertical skeletal elements are seen in sections, the entire lumen being occupied by large arched plates, which are not clearly divisible into dissepiments and tabulæ, but are arranged in concave floors, the concavity lessening towards the axis. The plates show little or no dilatation, and no trabeculæ can be seen on their surfaces.

Age. As these cystimorphs show neither trabeculæ nor dilatation, two characters important in indicating age, they are of no assistance in determining the age of the deposits, in which they are the commonest coral.

<div align="center">Family MYCOPHYLLIDÆ.</div>

Mycophyllidæ Hill, 1940.

<div align="center">Genus Pseudamplexus Weissermel.*</div>

Pseudamplexus Weissermel, 1897, p. 878.

Pselophyllum Počta, 1902, p. 82. Genolectotype, chosen Hill, 1940, *Pselophyllum bohemicum* Barrande in Počta, *id.*, Lower Devonian, F₂, Koněprus, Bohemia.

Genotype. Zaphrentis ligeriensis Barrois, 1889, p. 52, pl. iii, fig. 1, Lower Devonian, Erbray, France.

Diagnosis. Large, trochoid or sub-compound Rugosa with sub-equal short major and minor septa dilated and in contact to form a peripheral stereozone in lieu of a dissepimentarium, and with a wide tabularium of distant, horizontal, complete tabulæ.

Range. Lower Devonian of France, Bohemia and the Carnic Alps, Lower Middle Devonian of Silverwood, Queensland. Some of the species placed by Wedekind (1927, p. 37) in his genus *Pseudomphyma*, i.e. those species in which the calical rims are not expanded, from the Wenlock and Ludlow of Gotland, may be *Pseudamplexus*.

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* Lang, Smith and Thomas (1940, April 26, p. 108) have regarded *Pseudamplexus* Weissermel as a genus *caelebs*. But Hill (1940*a*, April 22, p. 158) had already accepted the genus, interpreting Weissermel's statements on p. 877 as placing *Z. ligeriensis* Barrois certainly in the genus.

Pseudamplexus princeps Etheridge.

(Plate III, figs. 1, 2.)

Tryplasma princeps Etheridge, 1907, p. 97, pl. xv, fig. 1 ;
pl. xvii, figs. 1–5 (*non* fig. 6) ; pl. xviii, figs. 1, 7 ;
pl. xix, figs. 1–3 ; pl. xx ; pl. xxi, figs. 1–9 ; pl. xxii,
figs. 1, 10 ; pl. xxiii, figs. 1–3. Molong and Wellington
Districts, New South Wales.

Lectotype (here chosen). F 35502 (Australian Museum),
Boree Ck. (either Portion 2, 3 or 12 $\frac{44}{1}$), Parish Cudal,
Co. Ashburnham ; Garra Beds, figured Etheridge, 1907,
pl. xviii, fig. 1 ; pl. xix, figs. 1–3.

Diagnosis. Sub-compound *Pseudamplexus* with relatively
narrow peripheral stereozone.

Description. The corallum may be solitary, or a sub-
compound corallum may be formed by the growth of one
or more series of offsets by peripheral increase after the
parent corallite has attained a large diameter, and as many
as 13 such offsets may arise at once from the one calice.
The individual corallites are conical at first and cylindrical
later, particularly those from which offsets do not arise.
One such individual was 25 cm. long, with diameter 55 mm.
Those individuals characterised by earlier increase are
conical rather than cylindrical, and usually somewhat
shorter. Most coralla are erect, but some are slightly
curved. Many possess rootlets ; the offsets may have
connecting processes. The epitheca shows well-marked
longitudinal ridges and furrows, the ridges usually broader
than the furrows ; growth annulation is also common,
and some few corallites show growth constrictions and
swellings.

There are between 70 and 80 septa about 3 or 4 mm.
long, the major being with difficulty distinguishable from
the minor. They are so dilated as to be in contact laterally
for half their length, and thus to form a peripheral stereozone
1 or 2 mm. wide—which of course appears wider in
tangentially weathered surfaces. This number of septa
is present very early, so that much of the later increase in
diameter of the corallum is accounted for by the increase
in the width of the septa, rather than by an increase in
their number. In some large corallites the septa may be
3 mm. wide at their bases, but a more usual width is 1 to
2 mm. In suitably broken specimens the septa are seen
to continue as thin, very low ridges on the upper surfaces

of the tabulæ, almost half-way to the axis, so that they must be amplexoid (Hill, 1935, p. 502). Whether they were better developed in the early stages of the corallum cannot at present be determined, as no tips of coralla are available. The micro-structure of the septa is as described for the genus (Hill, 1940a). They consist of a single series of rhabdacanths, much expanded laterally and very closely placed, fine lamellar sclerenchyme being interwoven with the "rods" of the rhabdacanths; but this growth-laminated sclerenchyme of each septum is not continuous with that of neighbouring septa. The tabulæ are thin, usually complete, and almost horizontal, but without great regularity; their spacing varies in different corallites, being as great as 4 mm., or as little as 1 mm. There are no dissepiments. The rootlets are hollow with a thick lining of lamellar sclerenchyme.

Remarks. The species resembles the Bohemian Lower Devonian (F_2) *P. obesus* Počta, 1902, pl. 32, figs. 16, 17) in the width of the stereozone, but differs in having the ability to produce offsets. It also resembles *Pseudomphyma profunda* Wedekind (1927, pl. 6, figs. 8–10) from the Ludlovian of Gotland, but has not the clear distinction between major and minor septa of the Gotland species. Etheridge compared his species to the Chinese Silurian *Amplexus appendiculatus* Lindström (1883, pl. vi, figs. 7, 8) but the similarities are not so great as those with the Lower Devonian *Pseudamplexus*.

Localities. In addition to the type locality, the species occurs at : 10 miles north of Molong on the Cumnock road (Por. 52, Par. The Gap) ; Mandagery's Ck., Por. 73 or 77, Par. Brymedura, probably Por. 73 ; Por. 31, Par. Bell ; Por. 174, Par. Bell (Crystal Springs) ; Por. 170, Par. Curra, near Wellington (Curra Ck. crossing).

Family RHABDOCYCLIDÆ.

Acanthocyclidæ Hill, 1936, p. 193.
Rhabdocyclidæ Hill, 1940b.

Genus Tryplasma Lonsdale.

Tryplasma Lonsdale, 1845, p. 613.
Tryplasma Hill, 1940b, *q.v.* for list of synonyms.

Genolectotype. *Tryplasma æquabile* Lonsdale, 1845, pp. 613, 633, pl. A, figs. 7, 7a. Silurian. River Kavka, near Bogoslovsk (east of the Northern Urals).

Diagnosis. Simple or fasciculate Rugose corals with a narrow peripheral stereozone of rhabdacanthine, holacanthine or dimorphacanthine septa in continuous lamellar sclerenchyme, the trabeculæ being free distally ; with complete tabulæ, and no dissepiments.

Range. Borkholm beds (Upper Ordovician or more probably Valentian of Estland), Silurian of Europe, Asia, America and Australia, and Lower Devonian of Europe and Australia.

Tryplasma columnare Etheridge.
(Plate III, figs. 3, 4.)

Tryplasma columnaris Etheridge, 1907, p. 85, pl. xv, fig. 6 ; pl. xix, fig. 5 ; pl. xxiv, figs. 2–5.   Garra Beds, Molong District, and Silurian of Quedong, Co. Wellesley, N.S.W.

Lectotype (here chosen).   F 35519, Australian Museum Collection, Garra Beds, Molong District (either Por. 4, Par. Boree Nyrang, or Boree Ck., Por. 2, Par. Cudal, Co. Ashburnham, N.S.W.), figured Etheridge, *loc. cit.*, pl. xix, fig. 5, being the only figured syntype not missing.

Diagnosis. Simple *Tryplasma*, with long, stout corallites (up to 25 mm. in diameter), and close, complete or incomplete tabulæ.

Description. The corallum is solitary, without offsets, turbinate at first, then long, cylindrical, straight or slightly curved, attaining a diameter of 25 mm.   The epitheca shows low, rounded longitudinal ridges, with (in Sydney University specimen 5169 from Nora Ck.) epithecal scales as described by Lindström.   Growth striæ and growth swellings and constrictions are characteristic.   There are 60 to 80 rhabdacanthine septa, forming a stereozone about 3 mm. wide, the minor septa being but little shorter than the major.   Trabeculæ may arise from the tabulæ. Both complete and incomplete tabulæ occur, so that the arrangement of these plates is somewhat irregular.   They are rather close.

Remarks. I have not seen the syntype from Quedong. Three specimens (Sydney University 5168–5170) have been collected from a new locality, Nora Ck., at the south end of Por. 191, Par. The Gap, Co. Ashburnham.   Somewhat slenderer corallites, of 15 mm. diameter (S.U. 5165) occur at the turn-off to Wellington Caves from the main road between Wellington and Molong, and are probably

referable to *T. columnare*. Other localities, in addition to the types, are 10 miles north of Molong on the Cumnock road (Por. 52, Par. The Gap); Por. 73 or 77 Par. Brymedura (Mandagery's Ck.); Por. 31, Par. Bell.

Family ENTELOPHYLLIDÆ.

Entelophyllidæ Hill, 1940.

Genus Entelophyllum Wedekind.

Entelophyllum Wedekind, 1927, p. 22.
Xylodes Lang and Smith, 1927, p. 461; Hill, 1940b.

Genotype by designation : *Madreporites articulatus* Wahlenberg, 1821 (1819), p. 97. Upper Silurian, Gotland.

Diagnosis. Compound Rugose corals typically with peripheral increase, long thin septa of which the major reach, or nearly reach the axis, an axial structure of axial tabellæ surrounded by concave periaxial tabellæ, and numerous, small, globose dissepiments.

Range. Wenlock and Ludlow of Europe, America and Australia. The species described below extends the range of the genus into the Lower Devonian.

Entelophyllum arborescens sp. nov.
(Plate III, fig. 5.)

Holotype. 6190, Sydney University Collection, from the Garra Beds (? Lower Devonian) of Nora Ck., Par. The Gap, near Molong, N.S.W., collected by Miss J. Johnston.

Diagnosis. Entelophyllum with xyloid septa, and with the tabulæ in a series of domes widely depressed axially.

Description. The corallum is large, fasciculate or partly cerioid, with individual corallites varying in diameter between 5 and 20 mm. ; their shape is not known owing to the massive nature of the rock containing them, but they are probably trochoid. Increase appears to be peripheral, the hystero-corallites tending to spread out one from another like the branches of a shrub. In a corallite 18 mm. in diameter there are 36 major septa extending about three-quarters of the way to the axis, being slightly turned aside from a radial course in the tabularium. They are rather ragged and a little thickened with xyloid carinæ in the disseptimentarium, but are thin and without carinæ in the tabularium. There are 36 minor septa, extending to the

inner edge of the dissepimentarium, *i.e.*, about half-way to the axis, with xyloid carinæ, but usually somewhat less thickened than the major septa.   The tabularium occupies half the diameter of the corallite.   The tabulæ are typically complete, domed, with a very wide axial sag, sometimes with a few supplementary tabellæ at the edge of the sag near the outer part of the tabularium.   The dissepiments are small and distally distended ; those of the outermost series may be rhomboid and rather large ; only the innermost series are steeply inclined.

Remarks.   The species differs from the genotype, to which it appears closer than to other known species, in the comparative simplicity of the axial structure, many of the tabulæ being complete, instead of being represented by numerous tabellæ as in the genotype.   The tabular floor is still a dome with an axial sag, but the axial sagging portion is wider than in *E. articulatus*.   The dissepiments are like those of *E. articulatus*.

MADREPORARIA TABULATA.

Family FAVOSITIDÆ.

Genus Favosites Lamarck.

Favosites Lamarck, 1816, p. 294.

Favosites Smith and Gullick, 1925, p. 117 ;   Jones, 1936, p. 2.

Genotype : Favosites gothlandicus Lamarck, 1816, p. 204, Silurian of Gotland.

Favosites allani Jones.

(Plate V, figs. 1*a*, 1*b*.)

Favosites allani Jones, 1937, p. 90, pl. xii, figs. 4, 5.

Diagnosis.   *Favosites* with small corallites, with numerous septal spines which are short, horizontal and with a broad base, with small circular mural pores typically in one row, and with thin, horizontal and usually complete tabulæ, 12 to 17 in 5 mm.

Description of a specimen from near Wellington (Sydney University 5181).   The corallites are of two sizes—1 to 1·5 mm. in diameter and 1·5 to 2 mm. in diameter, the former being triangular and hexagonal and the latter hexagonal to octagonal.   The walls are in the main moderately thin but across the section runs a band 10 to

15 mm. wide in which they are markedly thickened (up to 0·25 mm. thick). The septa consist of numerous short spines, horizontally directed or with a slight upward inclination. The mural pores are usually in one row but sometimes in two. The tabulæ are thin, complete and almost invariably horizontal ; they vary greatly in distance apart, there being 6 in 5 mm. in one part and 13 in 5 mm. in another part of the section.

Remarks. This specimen is quite typical of the species except in two characters—the walls are rather thicker even in the thinner walled part and much thicker in the thickened band, than in any other specimen we have examined ; and the tabulæ are more widely spaced. It should be noted that some specimens from the Upper Silurian of Yass have slightly thicker walls than that figured by Jones *loc. cit.*

Locality. Por. 50, Par. Curra, near Wellington, N.S.W. Mapping is being carried out in this area by Misses Basnett and Colditz and as yet the age of these limestones has not been established.

Favosites bryani Jones.
(Plate V, figs. 2a, 2b.)

Favosites bryani Jones, 1937, pp. 96-7, pl. xv, figs. 3-6.

Diagnosis. *Favosites* with small moderately thick walled polyhedric corallites, long, slender, sharply pointed septal spines, one row of circular mural pores, and fairly numerous tabulæ, which are mostly complete.

Description of the Molong specimen (University of Queensland Geological Museum, F.3503, two sections). The corallum is small, weathered and incomplete, but is flatly domed. The corallites are polygonal, octagonal to triangular, but usually hexagonal. The corallite walls are of a similar thickness to those of the holotype (Jones, *loc. cit.*, pl. xv, fig. 3) but the angles are slightly less rounded. The longitudinal section obtained is small and poor but a few long and slender septal spines of exactly the type illustrated in Jones' figures (*loc. cit.*, figs. 4, 6) can be seen. This section also shows the circular mural pores in one row and tabulæ as in the holotype but with a larger number inosculating.

Localities and Range. One of us has (Jones, *loc. cit.*) recorded this species from the Lower Middle Devonian of Good Hope near Yass, N.S.W., first limestone on the

Taemas Bridge Road from Yass, N.S.W., and of the limestones at the Yass end of the Taemas Bridge, N.S.W. ; the specimen here described is from Por. 3, Par. Cudal, near Molong, N.S.W.

FAVOSITES GOTHLANDICUS group and FAVOSITES
GOLDFUSSI.

The Silurian forms *Favosites gothlandicus* Lamarck, *Favosites forbesi* Edwards and Haime and *Favosites multiporus* Lonsdale have been fully discussed by one of us (Jones, 1936, pp. 2-14, text-figs. 1-12, pl. i) and shown to be conspecific. It was suggested that they be regarded as formæ distinguished as follows :

> *Favosites gothlandicus* Lamarck, forma *gothlandica* Lamarck, forms with no or very few septa and with thin walls.
>
> *F. gothlandicus* Lamarck, forma *forbesi* Ed. and H., forms with some septa and thicker walls.
>
> *F. gothlandicus* Lamarck, forma *multipora* Lonsdale, forms with many septa and with relatively thick walls.

It was further pointed out (*loc. cit.*, p. 14) that *F. maximus* Quenstedt, non Troost, is a form closely related to *F. gothlandicus* forma *gothlandica*, differing only in the size of the corallites.

The Middle Devonian *Favosites goldfussi* d'Orbigny was also discussed (*loc. cit.*, pp. 19-21, pl. ii, figs. 8-10). While it was recognised to be a variable form similar in many respects to some of the *gothlandicus* group, some specimens in particular closely resembling forma *forbesi* and forma *multipora*, though others have more thickened walls, rounded angles to the corallites and longer septa, it was kept as a separate species owing to the difference in age and the absence of connecting forms from the Lower Devonian. Comparatively few species of *Favosites* have been described from the Lower Devonian, the most being by Počta (1902), but his work was based mainly on externals and polished surfaces, so that exact comparison with other species is difficult. The Molong fauna described in this paper is probably of Lower Devonian age ; typical specimens of *F. gothlandicus* forma *gothlandica* and forma *forbesi* occur with others which might be placed either in

forma *multipora* or *F. goldfussi*. Two specimens in particular have long septa and rather rounded angles and are like those specimens of *F. goldfussi* which are less like forma *multipora*.

This suggests that *F. goldfussi* is a member of the *F. gothlandicus* group which survived into the Middle Devonian with only slight modifications.

In support of this idea the following observations are made : Some authors have regarded *F. goldfussi* as identical with, or as a variety of, *F. gothlandicus*, *e.g.* Nicholson (1879). The Middle Devonian form from the Eifel (consisting of small coralla with corallites of two sizes as is common in forma *forbesi*) has been regarded as a variety— var. *eifelensis*—of *F. goldfussi* by some authors, and by others as a separate species—*F. eifelensis* ; there are in the University of Queensland collection numerous specimens of this form from Auburg in the Eifel, some of which show little rounding of the angles and comparatively short septa so that they might equally well be referred to *F. gothlandicus* forma *forbesi*. The specimen from the Middle Devonian of the Eifel figured by Penecke (1894, p. 604, pl. ix, figs. 5, 6) as *F. eifelensis* is fairly thin walled and has fairly short septa, and it might easily be placed in *F. gothlandicus* forma *forbesi*. Other Devonian forms which may be related to the *F. gothlandicus* group are *F. graffi* Penecke (1897, p. 604, pl. ix, figs. 7-9 ; pl. xi, fig. 8) from the Middle Devonian, which is like *F. eifelensis* but has no septa ; *F. styriacus* Penecke (1894, p. 603, pl. ix, figs. 3, 4) from the Lower and Middle Devonian which is like *F. gothlandicus* forma *multipora*, but has smaller corallites ($1 \cdot 25$ to $1 \cdot 5$ mm. in diameter) and shorter septa ; *F. bohemicus* Barrande, Počta (1902, p. 241, pl. 85, figs. 1-9 ; pl. 106, figs. 3, 4) from the Lower and Middle Devonian which is very like a large *F. gothlandicus* forma *gothlandica* and probably should be referred to that species ; *F. helderbergiæ* Hall, Loewe (1914, p. 15, pl. iv, figs. 4*a-e*) from the Devonian of Ellesmereland which is like *F. gothlandicus gothlandica* with corallites 2 mm. in diameter and 4 to 7 tabulæ in 3 mm.

Summarising, the evidence points to *F. goldfussi* being a member of the *F. gothlandicus* group but is insufficient at present to merge *F. goldfussi* in forma *forbesi* and forma *multipora*. Two specimens from Molong are placed in

F. goldfussi and the remainder in the *F. gothlandicus* group.[1]

F. gothlandicus Lamarck, forma **gothlandica** Lamarck.

(Plate V, figs. 3*a*, 3*b*.)

Favosites gothlandica Lamarck, 1816, vol. ii, p. 206.

Favosites gothlandica Smith and Gullick, 1925, p. 118, pl. viii, fig. 1.

Favosites gothlandicus forma *gothlandica* Jones, 1936, p. 8, pl. i, figs. 1-4 ; Jones, 1937, p. 86, pl. xi, figs. 1, 2.

For description and figures, see Jones, 1936 and 1937.

Localities. Garra Beds of Por. 31, Par. Bell, Molong District ; Por. 81, Par. Bell, Molong District ; Por. 52 (probably), Par. Eurimbula, The Gap, near Molong, N.S.W. Also from the limestone in Pors. 46, 47 and Reserve, Par. Burrawang, Molong District, horizon unknown.

Favosites gothlandicus Lamarck forma **forbesi**

Edwards and Haime.

(Plate V, figs. 4*a*, 4*b*.)

Favosites forbesi Edwards and Haime, 1851, pp. 238-9 ; 1855, pp. 258-9, pl. lx, figs. 2, 2*a-e*, 2 *g* (excluding 2*f*).

Favosites gothlandicus Lamarck forma *forbesi* Edwards and Haime, Jones, 1936, pp. 9-12, pl. 1, figs. 5-7.

For description and figures see Jones, 1936.

Localities. Por. 171, Par. Curra, near Wellington, N.S.W. ; Por. 31, Par. Bell, near Garra, N.S.W. ; Por. 73 or 77 (probably 73), Par. Brymedura, Molong District— all University of Queensland Collection. Crystal Springs, west of Molong, N.S.W. (University of Sydney Collection sections 714, 715). Cudal, near Molong (U.S. section 708).

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[1] Since the above was written a paper by M. Lecompte (1939, " Les Tabules Dévonien moyen et supérieur du Bord sud du Bassin de Dinant ", *Mem. Mus. Roy. Hist. Nat. Belg.,* 90, 227 pp., 22 pls.) has come to hand. Lecompte suggests (p. 88) that *F. goldfussi* may be a descendant of the *F. gothlandicus* group, but states that with the Silurian material available to him he does not feel justified in assuming a relation.

Favosites gothlandicus Lamarck forma **multipora**, Lonsdale.

(Plate VI, figs. 1*a*, 1*b*.)

Favosites multipora Lonsdale, 1839, p. 683, pl. xv, bis, figs. 5, 5*c*, not necessarily figs. 5*a*, 5*b*.

Favosites multipora Edwards and Haime, 1851, p. 237.

Favosites forbesi (partim) Edwards and Haime, 1855, p. 258, pl. lx, fig. 2*f* only.

Favosites gothlandicus forma *multipora* Jones, 1936, pp. 13-14, pl. i, figs. 8-12.

For description and figures, see Jones, 1936.

Localities. Por. 3, Par. Cudal, near Molong ; Por. 73 or 77 (probably 73), Par. Brymedura, north of Garra, N.S.W. (University of Queensland Collection).

Favosites goldfussi d'Orbigny.

(Plate VI, figs. 2*a*, 2*b*.)

Favosites goldfussi (*partim*) d'Orbigny, 1850, p. 107 (fig. 3*b* of Goldfuss, 1892, only).

Favosites forbesi Edward and Haime var. *eifelensis* Nicholson, 1879, p. 61, pl. ii, fig. 3 ; pl. iii, figs. 1, 1*a-b*.

Favosites gothlandica Etheridge, 1899, p. 162, pls. xxii, xxiii.

Favosites goldfussi Jones, 1936, pp. 19-21, pl. ii, figs. 8-10 ; Jones, 1937, pp. 94-95, pl. xiii, fig. 6 ; pl. xiv, fig. 1.

For description and figures, see Jones, 1936 and 1937.

Localities. Por. 3, Par. Cudal, near Molong ; Por. 73 or 77 (probably 73), Par. Brymedura near Garra, N.S.W.

FAVOSITES NITIDUS–FAVOSITES SALEBROSUS group.

Favosites salebrosus Etheridge (1899) and *Favosites nitidus* Chapman (1914) have been briefly dealt with by one of us (Jones, 1937) and the resemblance of *F. nitidus* to *F. salebrosus* was pointed out. The examination of more of Chapman's material and of specimens from Molong, N.S.W., has convinced us that they are best regarded as the end members of a group and that forms occur which in some or all characters are intermediate between the two. Both species are very variable in almost all characters, but *salebrosus* is distinguished by having a considerable number of reclined corallites, which as a result are alveo-

litoid in transverse section ; again, polygonal corallites have the angles rounded. In *F. nitidus* the diameter of the corallites is more variable, 0·5 mm. to 0·75 mm., while in *salebrosus* it is fairly consistently 0·5 mm. None of Chapman's specimens of *nitidus* which we have seen show reclined or alveolitoid corallites, but all are small fragments.

A comparison may be drawn with *Favosites intricatus* Barrande, Počta (1902). The figures, pl. 88, figs. 11, 12, 15. 16 ; pl. 91, fig. 11, are of specimens with external form similar to *F. nitidus*, while the figures, pl. 95, figs. 1, 2, 4, 6, 11 show specimens with external form similar to *F. salebrosus*. This species differs, however, in internal characters (see Table 1). All the figured specimens were from Koneprus and of Lower Devonian age, whereas there is an age variation in the *F. nitidus-F. salebrosus* group from Upper Silurian [? Lower Devonian[1]] (*F. nitidus*) to Middle Devonian (*F. salebrosus*). *F. proasteriscus* Charlesworth (1914, p. 373, pl. xxxiii, figs. 1*a*, 1*b*) is described as having " undulating " corallites (? reclined) but no mention is made of, nor do the figures show, any alveolitoid corallites ; the species has no septa, close tabulæ and one row of large mural pores. It is from the Lower Devonian of the Carnic Alps. *F. salebrosus* has been adequately described by one of us (Jones, 1937, p. 95) except that mention was not made of the reclined position of many corallites. The feature is common to all specimens we have seen from the Woolomol, Moore Creek, and Nundle road limestones. It is possible, as has been suggested to us by Dr. Stanley Smith of Bristol, that the reclined posture of the corallites, with which is correlated the alveolitoid shape of the calices, may be the expression of an alveolitoid trend which may have acted in *Favosites* many times, producing species which have been referred to *Alveolites*. Thus *Alveolites* would be a polyphyletic genus.

We now propose to make a new variety of *F. nitidus* for the Molong form. *F. nitidus* will first be redescribed in more detail. See Table 1 for comparison with other species.

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[1] The Deep Creek fauna contains a species of *Prismatophyllum* Simpson which suggests a Lower Devonian age, but the fauna needs further investigation.

TABLE 1.—*Comparison of Various Species of Favosites.*

Species.	Size of Corallites (mm.).	Form of Corallites.	Walls.	Septa.	Mural Pores.	Tabulæ.	Range.
F. omsigorus sp. nov.	1·0	Polyhedric ir-regular in shape.	Thin or moderately thin.	None.	One row, very large, usually oval.	Complete 5–8 in 5 mm.	Lower Devonian in Australia.
F. alleni Jones.	1·0–2·0	Polyhedric ir-regular in shape.	Thin.	Numerous, short.	Usually one row, small circular.	Usually complete horizontal 11–17 in 5 mm.	Upper Silurian in Australia.
F. regularis Jones.	0·75–1·0	Polyhedric, regular in shape.	Slightly thickened.	Horizontal spines with broad base, variable in length.	Usually two rows, small circular.	Thin horizontal complete, 15–20 in 5 mm.	Upper Silurian in Australia.
F. gussensis Jones.	0·75–1·0	Polyhedric, regular in shape.	Moderately thin.	Very short in-clined spines.	Usually three rows, small circular.	22–35 in 5 mm.	Upper Silurian in Australia.
F. ottilie Penecke	0·5–0·75	Polyhedric, regular in shape.	Moderately thin.	None.	One row, fairly small, circular.	Complete about 18 in 5 mm.	Lower and Middle Devonian, Europe.
F. ottilie Penecke, specimen figured by le Maître.	0·75–1·25	Polyhedric, regular.	Moderately thick.	None.	One row "large", circular, numerous.	Complete, about 15 in 5 mm.	Transition beds between Lower and Middle Devonian in France.
F. alpinus R. Horn m s. Penecke.	Some 0·5 Most 0·75	Polyhedric, regular.	Thin.	Numerous short horizontal spines.	?	Thin, horizontal or inclined complete, occasionally inos-culating 10–14 in 5 mm.	Lower Devonian in Europe.
F. alpinus speci-men figured by le Maître.	0·75–1·0	Polyhedric, regular.	Moderately thin.	Fairly long hori-zontal spines of the type of *F. labrata* Jones not so numerous as in Penecke's figures	One row ?, cir-cular? similar to those in *inos-culans.*	Thin, horizontal or slightly concave about 6 in 5 mm.	Transition beds between Lower and Middle Devonian in France.
F. inoculans Nicholson, specimen figured by le Maître.	0·5	Polygonal to alveo-litoid with the angles rounded.	Fairly thick.	None	One row circular often near the angles so that three corallites communicate with one another.	Thin, horizontal inclined some-times incomplete and inosculating about 3 in 5 mm.	Transition beds between Lower and Middle Devonian in France.

TABLE 1.—*Comparison of Various Species of Favosites.*—Continued.

Species.	Size of Corallites (mm.).	Form of Corallites.	Walls.	Septa.	Mural Pores.	Tabular.	Range.
F. basalticus Goldfuss.	2·0	Polyhedric, regular in shape.	Moderately thin.	None.	Usually one row, occasionally two, 0·25 to 0·4 mm. in diameter.	Complete horizontal 9 in 5 mm.	Devonian.
F. salebrosus Edheridge.	0·5	Polyhedric or rounded, frequently reclined, and alveolitoid.	Moderately thick.	Few, short, blunt spines.	One row, large circular.	7 in 5 mm., complete thin, horizontal or inclined.	Middle Devonian in Australia.
F. intricatus Barrande; Počta.	1·0	Some specimens erect and polyhedric, others reclined and alveolitoid in parts.	Thin in some, moderately thick in others.	From the figures none in specimens, many in others.	One, sometimes two, rows, circular.	Complete 35 in 1 cm. (misprinted 1 mm.).	Lower Devonian.
F. prosalericus Charlesworth.	About 1·0	Polyhedric, undulating.	Moderately thin.	None.	Large, circular, one row.	Complete, 12 in 5 mm.	Lower Devonian, Europe.
F. nitidus Chapman.	0·5 -0·75	Erect and polyhedric or with angles a little rounded; reclined and alveolitoid very rare or absent.	Moderately thick.	Numerous in parts of corallum. Short, blunt spines with broad base.	One row, circular, large, more numerous than in *F. salebrosus*.	Usually complete, some inosculating 15-20 in 5 mm.	Upper Silurian [?Lower Devonian].
F. nitidus Chapman var. **medius** var. nov.	0·5 a few 0·75	Most erect and polyhedric, angles slightly or not at all rounded. A few reclined and alveolitoid.	Slightly thickened.	Sparsely distributed short, blunt spines with broad base.	One row, large, circular, more numerous than in *F. salebrosus*.	Complete, thin, usually horizontal, sometimes reclined 7-9 in 5 mm. in some specimens, 15-19 in 5 mm. in other specimens.	Lower Devonian in Australia.
F. bryani Jones	1·0	Polyhedric or with angles slightly rounded, regular.	Moderately thick.	Long slender pointed spines.	Medium size, one row, circular.	Usually complete, some inosculating 17 in 5 mm.	? Lower Middle Devonian in Australia.

Favosites nitidus Chapman.

(Plate VI, figs. 3a, 3b, 3c.)

Favosites nitida Chapman, 1914, p. 309, pl. liv, figs. 21-23 ;
    pl. lv, figs. 24, 25.

Favosites nitida Jones, 1937, p. 93, pl. xii, figs. 4, 5.

Lectotype. Chapman, *loc. cit.*, did not choose a holotype,
but figured three cotypes (M.D. 564, M.D. 576 and M.D.
749) and two paratypes (M.D. 588 and M.D. 592), all from
Deep Creek, Thomson River, Gippsland, Victoria, except
M.D. 749, which is from Cooper's Creek, Gippsland, Victoria.
We choose as lectotype the specimen in the National
Museum, Melbourne, M.D. 749 with two slides 1335, from
Cooper's Creek, Walhalla, Victoria.

Diagnosis. Favosites with small, erect polyhedric coral-
lites, blunt septal spines which are very irregularly
distributed and may be entirely absent in parts of the
corallum, one row of large circular mural pores and fairly
numerous complete tabulæ.

Description of the lectotype. The external form of
the corallum is unknown. The corallite walls are usually
moderately thick ; the corallites are erect and polygonal
and are usually polyhedric but the angles may be a little
rounded ; alveolitoid corallites are rare or entirely absent.
The diameter of the corallites is 0·5 to 0·75 mm. The
septal spines are numerous in some parts of the corallum,
but may be entirely absent in other parts ; they are short
blunt spines with a broad base, and a slight upward
inclination. The mural pores are in one row which may
be sinuous ; they are large and close together—0·4 to
0·5 mm. between their centres. The tabulæ are thin,
usually complete, occasionally incomplete and inosculating,
horizontal or oblique, three or four in one millimetre.

Localities and Age. Deep Creek, Thomson River,
Victoria, and Cooper's Creek, Victoria. Upper Silurian
[? Lower Devonian.]

Favosites nitidus Chapman var. **medius** var. nov.

(Plate VI, figs. 4a, 4b ; Plate VII, figs. 1a, 1b, 2.)

Holotype. 5178, with two sections (Sydney University
Collection), Por. 51, Par. Eurimbula, between Wellington
and Molong, N.S.W.

Diagnosis. Favosites with the external form of *F.
nitidus* but with a few corallites alveolitoid ; with the

internal characters of *F. salebrosus*, but some with more numerous tabulæ.

Description. The external form is unknown, but nearly all the corallites are erect, only a few being reclined, the diameter of the corallites is 0·5 mm., with a few 0·75 mm. The walls of the corallites are slightly thickened but the angles are only slightly or not at all rounded. Only a few corallites are alveolitoid. The septa vary considerably in number in different parts of the corallum, but mostly they are sparsely distributed. They are short blunt spines with a broad base, upwardly inclined or almost horizontal, but in some parts they may be fairly numerous, longer and curved. The mural pores are large and circular, in one row. The tabulæ are complete, usually horizontal, sometimes inclined or concavo-convex, in some specimens 7 to 9 in 5 mm. (like *salebrosus*), in others 15 to 19 in 5 mm. (like *nitidus*).

Localities and Age. Por. 3, Par. Cudal, near Molong; Mandagery's Creek, probably Por. 77, Par. Brymedura, near Molong; Por. 51, Par. Eurimbula, between Wellington and Molong. Probably Lower Devonian.

Favosites ovatiporus sp. nov.

(Plate VII, figs. 3a, 3b, 4a-c; Plate VIII, figs. 1, 2a, 2b.)

Holotype. Specimen in the University of Sydney Geological Museum F.5177, with (two sections) from Por. 184, Par. Cudal, near Molong, N.S.W.

Diagnosis. *Favosites* with small corallites, no septa, and very large usually oval mural pores; tabulæ complete, rather distant.

Description. The external form of the corallum is unknown. The corallites are mostly five- or six-sided, polyhedric, 0·75 to 1·5 but the majority 1 mm. in diameter, with walls thin or slightly thickened; the sides of the corallites are unequal, so that the shape is irregular. There is no trace of septa. The mural pores are in one row, very large and usually oval, the vertical axis being the longer, but a few are circular or almost circular. The size of the pores varies greatly but usually they are almost or quite as wide as the face they occupy. The long axis of the oval ones is about 1 mm. When smaller than the width of the face they may occupy any position on the face. The tabulæ are complete horizontal or inclined, 5 to 8 in a space of 5 mm.

Remarks. The very large usually oval mural pores (see Plate VIII, fig. 1) are a striking feature of the species and distinguish it from all other species we know. In transverse section one-half to the whole of sides of corallites is frequently missing as a result of the large size of the pores.

One specimen from Parish Cudal (University of Sydney Geological Department Slides 706–707) shows an unusual character. In the transverse section approximately half the section shows adult corallites with a diameter of 1 to 1·5 mm. while the other half has corallites with a diameter 0·5 to 0·75 mm. (see pl. vij, fig. 4a). The change from one size to the other is not gradual but quite sudden. This is probably the result of a difference in the environment (food supply ?, light ?) of one part of the corallum to that of the other part. Another transverse section cut from a different part of the specimen shows corallites of only the normal size.

Table 1 gives a comparison of this species with others which present any character in common with it.

Localities and Age. Por. 184, Par. Cudal, near Molong (S.U. 5177); Par. Cudal near Molong (S.U. slides 706, 707); Por. 3, Par. Cudal, near Molong (University of Queensland) ; all probably Lower Devonian. Loyola, near Mansfield, Victoria (University of Queensland), Lower Devonian.

Genus Striatopora Hall.

Striatopora Hall, 1851, p. 400.

Genotype. *Striatopora flexuosa* Hall, 1851, p. 400, Niagaran, New York.

Striatopora sp.

(Plate VIII, figs. 3a, 3b, 3c.)

A single specimen from Crystal Springs (Por. 174, Par. Bell) near Molong probably belongs to *Striatopora*, but we do not propose to give it a specific name as the genus is much in need of revision. The corallum is cylindrical and branches dichotomously, the branches having a diameter up to 18 mm. The internal characters are illustrated by the figures. *Striatopora* occurs in the Silurian and Devonian.

Family SYRINGOPORIDÆ.

Genus Syringopora Goldfuss.

Syringopora Goldfuss, 1826, p. 75.

Genotype. *Syringopora ramulosa* Goldfuss, Carboniferous, Olne near Limburg, Germany.

Syringopora sp.
(Plate VIII, fig. 4.)

Two specimens from Crystal Springs near Molong (Por. 174, Par. Bell) belong to *Syringopora* Goldfuss. This genus is in need of revision and we do not propose to give the specimens a trivial name at present. *Syringopora* ranges from the Upper Ordovician to the Carboniferous.

MADREPORA HELIOLITIDA.

Family HELIOLITIDÆ.

Genus Heliolites Dana.

Heliolites Dana, 1846, p. 541 ; Lindström, 1899, p. 38 ; Jones and Hill, 1940, p. 198.

Genotype. *Astræa porosa* Goldfuss, 1826, p. 64, pl. xxi, fig. 7, Devonian of the Eifel.

Heliolites daintreei Nicholson and Etheridge.
(Plate VIII, fig. 5.)

Heliolites daintreei Nicholson and Etheridge, 1879, p. 224, pl. xiv, figs. 3, 3a. Devonian, Broken River, North Queensland, Jones and Hill, 1940, p. 199.

Lectotype. 90248, British Museum (Natural History).

Diagnosis. *Heliolites* with tabularia of variable size, with twelve short lamellar septa having numerous long upcurved spines vertical near the axis and swollen at their apices in late forms ; with distant, regularly horizontal tabulæ ; with tubuli regularly polyhedric or vermiform, sometimes rounded in late forms ; and with the walls of the tabularia rather thickened in late forms.

Remarks. This species, including the Molong specimens, is described in a paper on the Heliolitida in the Proceedings of the Royal Society of Queensland (Jones and Hill, 1940), where we show it to be divisible into four ill-defined groups.

The Molong specimens are placed in a group with others from the Upper Silurian of Yass and the Devonian of Broken River, North Queensland.

Locality. Por. 3, Par. Cudal, just west of Boree Ck. on back road from Manildra to Cudal, near Molong, N.S.W.

Genus Plasmopora Edwards and Haime.

Plasmopora Edwards and Haime, 1849, p. 262 ; Lindström, 1899, p. 75 ; Jones and Hill, 1940, p. 204.

Genotype. *Porites petaliformis* Lonsdale, 1839, p. 687, pl. xvi, figs. 4, 4*a*, from the Wenlock shale, Walsall, England.

Plasmopora gippslandica (Chapman).

(Plate VIII, fig. 6.)

Heliolites interstincta var. *gippslandica* Chapman, 1914, p. 331, pl. lx, figs. 35, 36. Silurian, [? Devonian], Cooper's Ck., Thomson River, Victoria.

Plasmopora gippslandica (Chapman), Jones and Hill, 1940, p. 206.

Holotype. MD. 746, with slide 1336, National Museum, Melbourne.

Diagnosis. *Plasmopora* with the tubûli of the aureola usually elongated radially ; neighbouring aureolæ in contact, or occasionally separated by one or two rows of tubuli ; tubuli walls continuous vertically ; septa absent.

Remarks. The specimens from Molong are described with others in a paper on the Heliolitida (Jones and Hill, 1940). The species is known elsewhere from the Devonian of Johannsen's Caves near Rockhampton, Queensland, and of the Nundle road near Tamworth, N.S.W., and from the Upper Silurian of Yass, in addition to the type locality.

Localities in the Garra Beds. Pors. 37 and 174, Par. Bell, Co. Ashburnham, near Molong ; Por. 170, Par. Curra, near Wellington. Probably Lower Devonian.

Summary.

In this paper the coral fauna of the Garra Beds is described. It contains four new species, one new variety and fourteen other forms known elsewhere in the Silurian, Lower or Middle Devonian, and is in all probability Lower Devonian. European species of *Favosites* and *Heliolites* occur.

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EXPLANATION OF PLATES.

PLATE II.

Rugosa of the Garra Beds, N.S.W.

All figures approximately ×2 diameters, except where otherwise indicated.

Acanthophyllum sp.

Fig. 1.—Holotype, 5171, Sydney University Collection, Por. 81, Par. Brymedura. Transverse section.

Fig. 2.—F.3491, University of Queensland Collection, 10 miles north of Molong, on the Cumnock road, probably Por. 52, Par. The Gap. *a*, transverse section; *b*, vertical section.

Rhizophyllum enorme Etheridge.

Fig. 3.—F.3488, University of Queensland Collection, Por. 3, Par. Cudal, Boree Ck. External view, ½ natural size.

Fig. 4.—F.3489, University of Queensland Collection, Por. 3, Par. Cudal, Boree Ck. *a*, transverse section; *b*, vertical section.

" *Cystiphyllum* " sp.

Fig. 5.—F.3485, University of Queensland Collection, Curra Ck. crossing, Por. 170, Par. Curra near Wellington. Transverse section.

Fig. 6.—F.3486, University of Queensland Collection, Curra Ck. crossing, Por. 170, Par. Curra near Wellington. Vertical section.

PLATE III.

Rugosa of the Garra Beds, N.S.W.

All figures approximately ×2 diameters, except where otherwise indicated.

Pseudamplexus princeps (Etheridge).

Fig. 1.—F.3480, University of Queensland Collection, Mandagery's Ck., Por. 73 or 77, Par. Brymedura. Natural size.

Fig. 2.—Doubtfully identified with this species, F.3483, University of Queensland Collection, Curra Ck. crossing, Por. 170, Par. Curra near Wellington. *a*, transverse section; *b*, vertical section.

Tryplasma columnare Etheridge.

Fig. 3.—F.3492, University of Queensland Collection, 10 miles north of Molong on the Cumnock road, probably Por. 52, The Gap. Transverse section.

Fig. 4.—From F.3510, University of Queensland Collection, Por. 31, Par. Bell. Part of vertical section.

Entelophyllum arborescens sp. nov.

Fig. 5.—Holotype 6190, Sydney University Collection, Nora Ck., Par. The Gap.

PLATE IV.

Rugosa of the Garra Beds, N.S.W.

Figures approximately ×2 diameters.

Spongophylloides (?) *thomasæ* sp. nov.

Fig. 1.—NS.1296, Sydney University Collection, holotype, near Cudal. *a*, transverse section ; *b*, vertical section.

PLATE V.

Tabulata of the Garra Beds, N.S.W.

Figures approximately ×2 diameters.

Favosites allani Jones.

Fig. 1.—5181, Sydney University Collection, Por. 50, Par. Curra. *a*, transverse section ; *b*, vertical section.

Favosites bryani Jones.

Fig. 2.—F.3503, University of Queensland Collection, Mandagery's Ck., probably Por. 73, Par. Brymedura. *a*, transverse section ; *b*, vertical section.

Favosites gothlandicus Lamarck forma *gothlandica* Lamarck.

Fig. 3.—F.3469, University of Queensland Collection, 20 miles north of Molong on the Cumnock road (limestone in Pors. 46, 47 and Reserve, Par. Burrawang). *a*, transverse section ; *b*, vertical section.

Favosites gothlandicus Lamarck forma *forbesi* Edwards and Haime.

Fig. 4.—F.3474, University of Queensland Collection, Curra Ck. crossing, Por. 170, Par. Curra. *a*, transverse section ; *b*, vertical section.

PLATE VI.

Tabulata of the Garra Beds, N.S.W., and of Cooper's Ck., Victoria.

Figures approximately ×2 diameters.

Favosites gothlandicus Lamarck forma *multipora* Lonsdale.

Fig. 1.—F.3493, University of Queensland Collection, Mandagery's Ck., probably Por. 73, Par. Brymedura. *a*, transverse section ; *b*, vertical section. Neither of these photographs shows as many septal spines as the sections.

Favosites goldfussi d'Orbigny.

Fig. 2.—F.3496, University of Queensland Collection, Mandagery's Ck., probably Por. 73, Par. Brymedura. *a*, transverse section ; *b*, vertical section.

Favosites nitidus Chapman.

Fig. 3.—Holotype MD.749, National Museum, Melbourne, Cooper's Ck., Walhalla, Victoria. *a*, *b*, transverse section ; *c*, vertical section.

U—July 3, 1940.

Favosites nitidus Chapman var. *medius* var. nov.

Fig. 4.—Holotype, 5178, Sydney University Collection, Por. 51, Par. Eurimbula. *a*, transverse section ; *b*, vertical section.

PLATE VII.

Tabulata of the Garra Beds, N.S.W.

Figures approximately ×2 diameters.

Favosites nitidus Chapman var. *medius* var. nov.

Fig. 1.—F.3497, University of Queensland Collection, Mandagery's Ck., probably Por. 77, Par. Brymedura. *a*, transverse section ; *b*, vertical section.

Fig. 2.—F.3499, University of Queensland Collection, Boree Ck., Por. 3, Par. Cudal. Vertical section.

Favosites ovatiporus sp. nov.

Fig. 3.—Holotype, F.5177, Sydney University Collection, Por. 184, Par. Cudal. *a*, transverse section ; *b*, vertical section.

Fig. 4.—707 = 706, Sydney University Collection, Cudal. *a*, *b*, transverse section ; *c*, vertical section.

PLATE VIII.

Tabulata and Heliolitida from the Garra Beds, N.S.W., and from Loyola, Victoria.

Figures ×2 diameters, except where otherwise indicated.

Favosites ovatiporus sp. nov.

Fig. 1.—F.3501, University of Queensland Collection, Boree Ck., Por. 3, Par. Cudal. Vertical section.

Fig. 2.—F.3502, University of Queensland Collection, Loyola, Victoria. *a*, transverse section ; *b*, vertical section.

Striatopora sp.

Fig. 3.—F.3513, University of Queensland Collection, Crystal Springs, Por. 174, Par. Bell. *a*, natural size, external ; *b*, transverse section ; *c*, vertical section.

Syringopora sp.

Fig. 4.—5176, Sydney University Collection, Crystal Springs, Por. 174, Par. Bell. External view. Natural size.

Heliolites daintreei Nicholson and Etheridge.

Fig. 5.—F.3408, University of Queensland Collection, Boree Ck., Por. 3, Par. Cudal. Transverse section.

Plasmopora gippslandica (Chapman).

Fig. 6.—F.3510, University of Queensland Collection, Por. 31, Par. Bell. *a*, transverse section ; *b*, vertical section.

1a
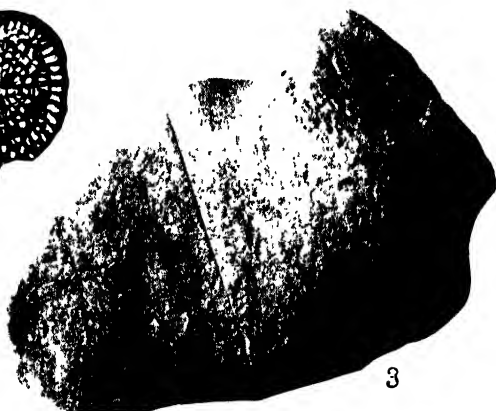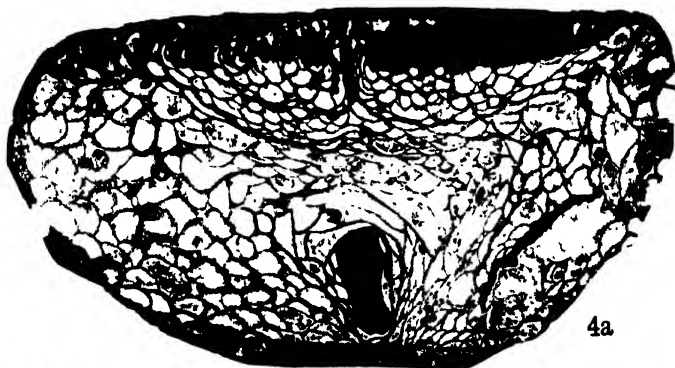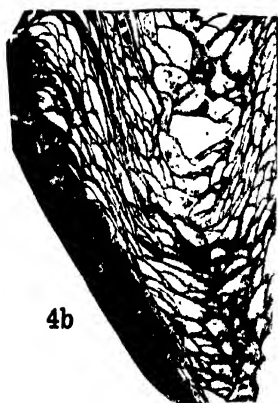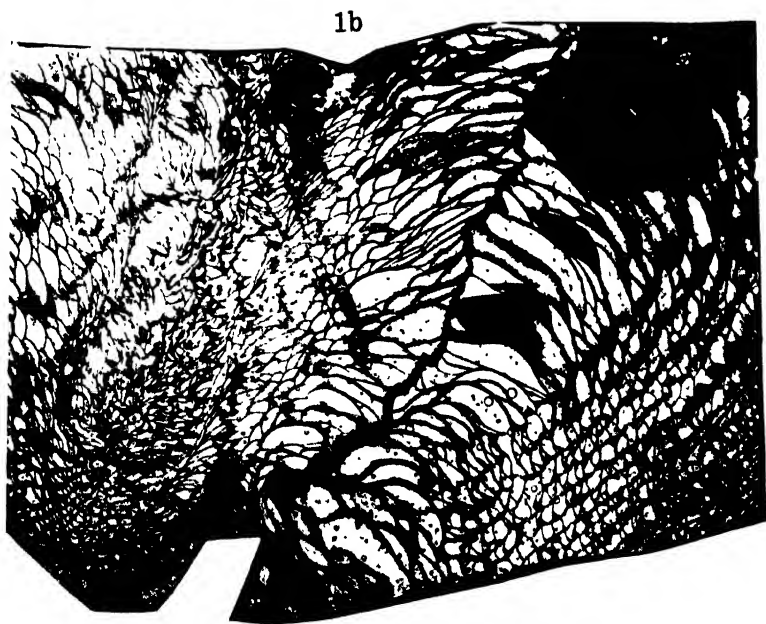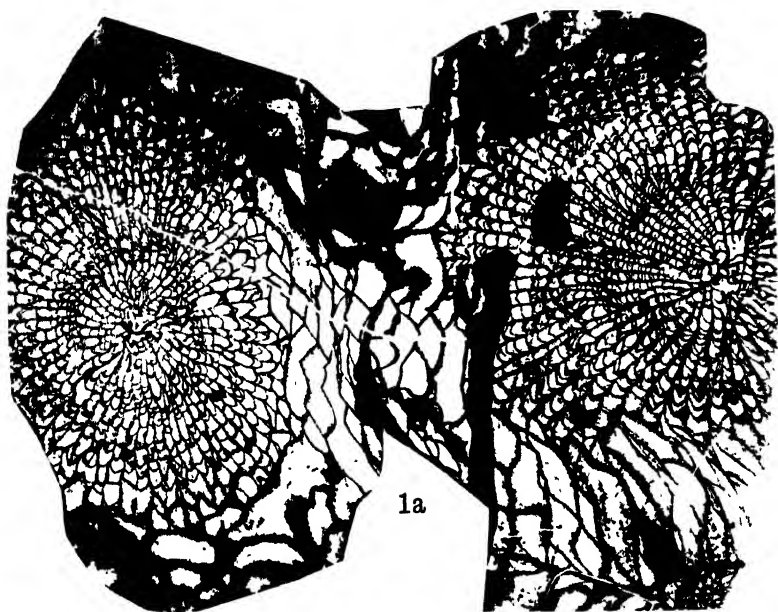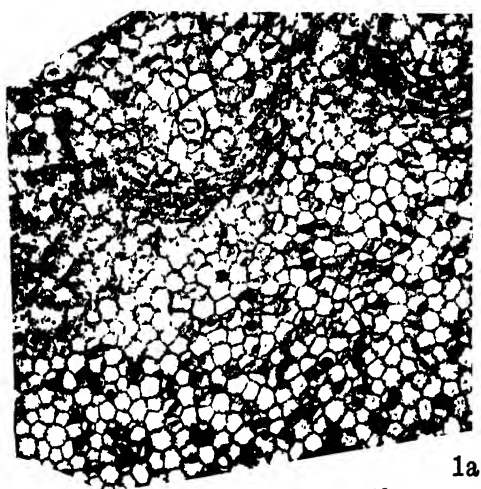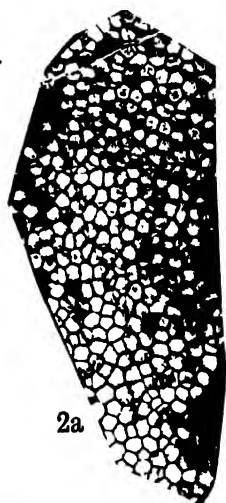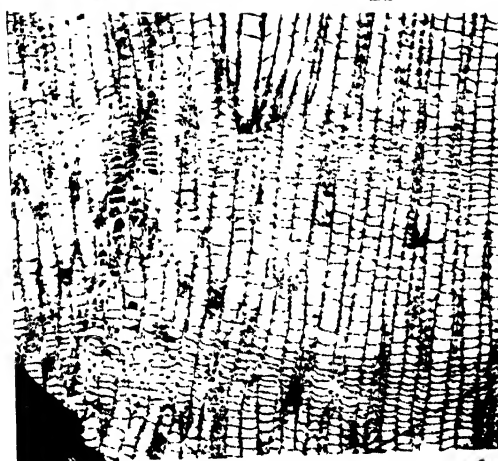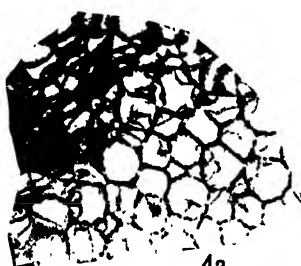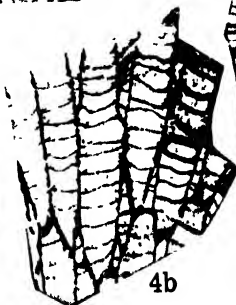
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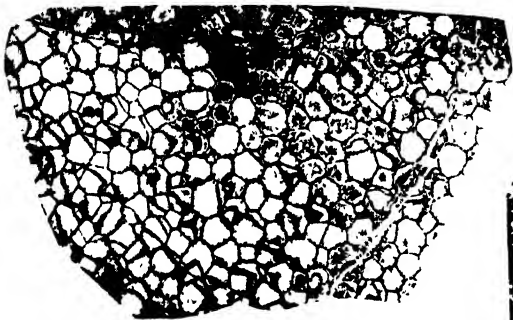
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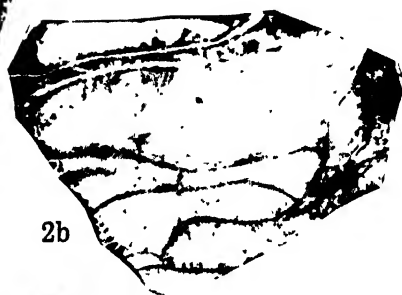
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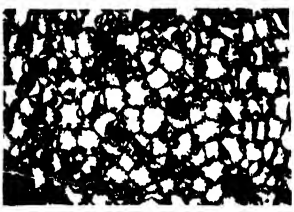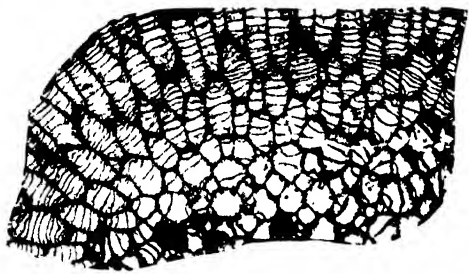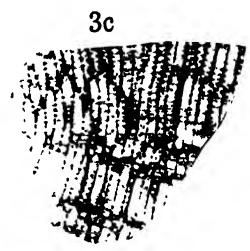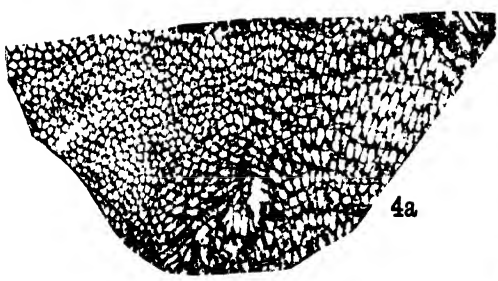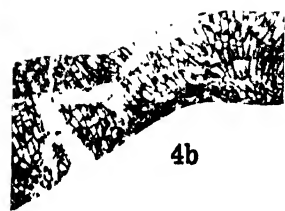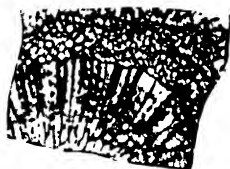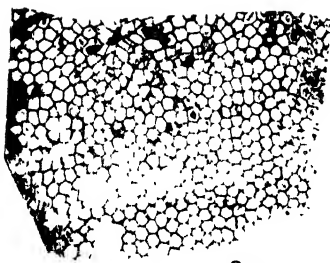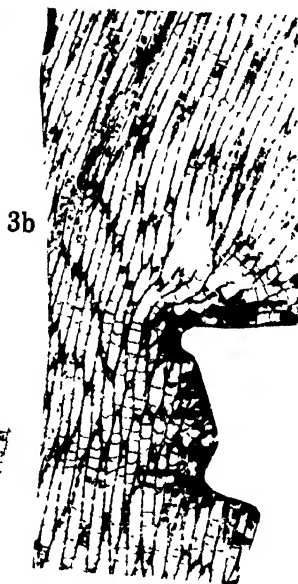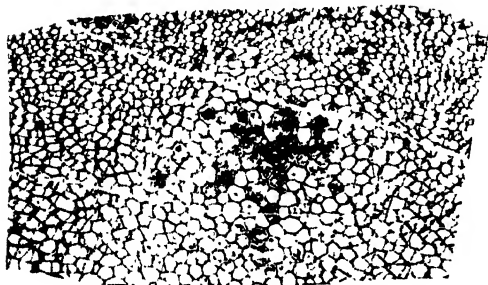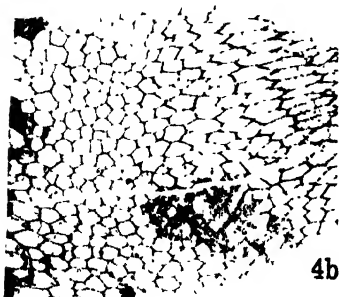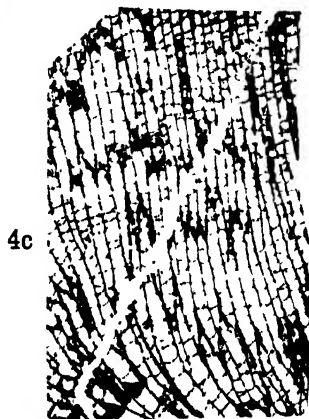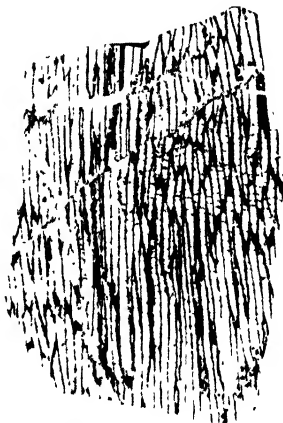
6 a

6 b

ELEMENTARY PRESENTATION OF THE FRE-QUENCY DISTRIBUTIONS OF CERTAIN STATISTICAL POPULATIONS ASSOCIATED WITH THE NORMAL POPULATION.

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(Communicated by PROFESSOR T. G. ROOM.)

The distributions of Helmert's χ^2, Student's t, R. A. Fisher's z, etc., are of interest in current statistical theory, and various proofs are now accessible.[1] [2] [3] [4] The cumulative frequencies for these distributions, however, may all be simply expressed as incomplete Eulerian integrals of either the second (Gamma) or the first (Beta) kind.[5] The quantities χ^2 and s^2 (an estimate of the variance of the parent normal distribution) are of the dimensions of the square of a normal variate and are expressible as Gamma variates. The square of Student's t, Fisher's z, and also the square of Cauchy's variate (the ratio of two random deviates in a normal distribution) are all ratios (representable as angular magnitudes) having no dimension in the parent variate, and are expressible as Beta variates.

I. EXPLANATORY.

We consider a collection or "population" of N magnitudes each satisfying some proposition of the type "X is the a of an O", e.g. X is the age of a man, whose

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[1] The Mathematical Distributions used in the Common Tests of Significance, R. A. Fisher in *Econometrica*, Vol. 3, No. 4, Oct., 1935.

[2] Introduction to Mathematical Probability, J. V. Uspensky, 1937, Chap. XVI.

[3] Random Variables and Probability Distributions, H. Cramer, 1937, Chap. V, Sec. 6 *et seq.* (Camb. Tract No. 36.)

[4] Statistical Mathematics, A. C. Aitken, 1939, Sec. 72, 74.

[5] Integral Calculus, Todhunter, 1878, Art. 256 *et seq.*

values in terms of a chosen unit range from α, the smallest, to λ, the largest; and such that the number of these magnitudes with values less than a particular value X_r is $N.F(X_r)$. $F(X_r)$ is thus the proportion or relative frequency of magnitudes with values less than X_r, and may be called the cumulative relative frequency, or, briefly, the cumulative frequency up to X_r. Naturally $F(\alpha)=0$, $F(X)$ never decreases as X increases from α to λ, and finally $F(\lambda')=1$, where λ' exceeds λ however slightly.

If $F(X)$, the cumulative frequency up to X, is a continuous differentiable function of X, and we can assume N to be as large as we please, we have a theoretical *continuous* frequency distribution. Taking the number of magnitudes with values from X up to $X+h$ as an integer differing little from $N\{F(X+h)-F(X)\}$, the relative frequency of magnitudes from X to $X+h$ is the proportion which this integer is of N. By taking N large enough, this proportion will differ from $F(X+h)-F(X)$ by as little as we please. When h is small enough $F(X+h)-F(X)=\dfrac{dF(X)}{dX}.h$ as nearly as we please, and, as h is the width of the interval, $\dfrac{dF(X)}{dX}$ is called the density of relative frequency, or, briefly, the frequency density, in the immediate neighbourhood of the value X. Conversely, denoting the frequency density by $f(X)$, the frequency with which the variate has values from X to $X+dX$ is $f(X)dX$. The cumulative frequency up to X is $F(X)=\displaystyle\int_{\alpha}^{X} f(X)dX$, and $\displaystyle\int_{\alpha}^{\lambda} f(X)dX=1$.

The class of objects under observation may be measurable in more than one particular. We then consider a collection of N *sets* of magnitudes, the components $X, Y, Z \ldots$ of each set satisfying some proposition of the type " X, $Y, Z \ldots$ are respectively the $a, b, c \ldots$ of an O ", e.g. $X, Y \ldots$ are respectively the lifting strength, length of foot $\ldots$ of a man. If we focus attention on those of the N sets in which Y has a particular value Y, the proportion of these sets in which X is less than a particular value X will often depend not only on X but also on Y. If, however, this proportion while dependent on X is independent of Y, then it has the same value, $F(X)$, for all of the N sets in

which Y is less than the value Y. If these form a proportion $G(Y)$ of the N sets, it follows that the proportion of the N sets in which X is less than the value X and Y is less than the value Y is $F(X).G(Y)$. Hence also $G(Y)$ is independent of the value of X and thus the frequency distribution of each variate is the same for every possible value of the other variate. The variates are then said to be *statistically independent*.

In the case of theoretical continuous distributions of two variates X and Y, if these are statistically independent, the frequency of sets in which the values of X are from X to $X+h$ and of Y from Y to $Y+k$ is $\{F(X+h)-F(X)\} . \{G(Y+k)-G(Y)\}$, or $\dfrac{dF(X)}{dX} . \dfrac{dG(Y)}{dY} . hk$ as nearly as we please if h and k are small enough.

Denoting the frequency densities by $f(X)$ and $g(Y)$, the frequency of sets in which X has values from X to $X+dX$ and Y has values from Y to $Y+dY$ is $f(X)dX . g(Y)dY$. The cumulative frequency up to X and up to Y is $\displaystyle\int_\alpha^X f(X)dX . \int_\beta^Y g(Y)dY$, and $\displaystyle\int_\alpha^\lambda f(X)dX = \int_\beta^\mu g(Y)dY = 1$, where the range of values of X is from α to λ, and of Y from β to μ.

Statistical dependence or independence is not concerned with the forms of $F(X)$ and $G(Y)$. For example F and G may be identical in form while X and Y are statistically independent. Again, it is not necessary that a linear or functional equation should exist among the variates in order that they may be statistically dependent. For example the variates $(x+y)$ and x are usually statistically dependent.

Abbreviations may be used as follows :
> f. =relative frequency.
> f.d. =relative frequency density.
> c.f. =cumulative relative frequency.

II. The Standard Gamma and Beta Distributions.

The positive variate u, whose c.f. is

$$F(u) \equiv \int_0^u \frac{1}{\Gamma(l)} e^{-u} u^{l-1} du,$$

is a standard Gamma variate, and may be denoted by $c(l)$.

As $\int_0^\infty e^{-u}u^{l-1}du = \Gamma(l)$, $F(u)$ ranges from 0 to 1 as u ranges

from 0 to ∞. $F(u)$ may be written as $\dfrac{\gamma(l)}{\Gamma(l)}$, where $\gamma(l)$ is the incomplete Gamma integral up to the particular value of u, and $\Gamma(l)$ is the complete Gamma integral, with parameter l.

If u and v form a set of two magnitudes appertaining to a member of a certain infinitely large population, and if u and v therein are statistically independent Gamma variates $c(l)$ and $c(m)$, the f. with which u has values from u to $u+du$ and v has values from v to $v+dv$ is

$$\frac{1}{\Gamma(l)\Gamma(m)}e^{-(u+v)}u^{l-1}v^{m-1}du\,dv \dots \dots \dots (1)$$

All the distributions which form the subject of these notes may be deduced from this compound frequency element by means of the transformation
$$u = \theta s, \quad v = (1-\theta)s.$$

Hence $u+v = s$, $\dfrac{u}{u+v} = \theta$, and $du\,dv = s\,d\theta\,ds$, and the element becomes

$$\frac{1}{\Gamma(l)\Gamma(m)}e^{-s}s^{l+m-1}ds\,.\,\theta^{l-1}(1-\theta)^{m-1}d\theta \dots \dots (2)$$

As this is of the form $f(s)ds\,.\,g(\theta)d\theta$, the new variates s and θ or $u+v$ and $\dfrac{u}{u+v}$ are statistically independent of one another. The range of s is from 0 to ∞, and of θ from 0 to 1.

As $\int_0^\infty e^{-s}s^{l+m-1}ds = \Gamma(l+m)$

and $\int_0^1 \theta^{l-1}(1-\theta)^{m-1}d\theta = \dfrac{\Gamma(l)\Gamma(m)}{\Gamma(l+m)}$,

and as (2) may be written as
$$\frac{1}{\Gamma(l+m)}e^{-s}s^{l+m-1}ds\,.\,\frac{\Gamma(l+m)}{\Gamma(l)\Gamma(m)}\theta^{l-1}(1-\theta)^{m-1}d\theta,$$
it follows that the c.f. of s or $(u+v)$ up to the particular

value s is $\int_0^s \dfrac{1}{\Gamma(l+m)}e^{-s}s^{l+m-1}ds$ or $\dfrac{\gamma(l+m)}{\Gamma(l+m)}$ $\dots \dots (3)$

and that the c.f. of θ or $\dfrac{u}{u+v}$ up to the particular value

θ is $\displaystyle\int_0^\theta \dfrac{\Gamma(l+m)}{\Gamma(l)\Gamma(m)}\theta^{l-1}(1-\theta)^{m-1}d\theta$ or $\dfrac{\beta(l,\,m)}{B(l,\,m)}$ .... (4)

where $\beta(l,m)$ denotes the incomplete, and $B(l,m)$ the complete Beta integral with parameters l,m. The variate θ is a standard Beta variate and may be denoted by $b(l,m)$. With these notations the result (3) may be briefly written .

$$c(l)+c(m)=c(l+m) \quad \dots\dots\dots\dots\dots\dots (5)$$

or stated in words : the frequency distribution of the sum of two statistically independent Gamma variates with parameters l and m is that of the Gamma variate with parameter $(l+m)$.

Likewise the result (4) may be briefly written

$$\frac{c(l)}{c(l)+c(m)}=b(l,m) \quad \dots\dots\dots\dots\dots\dots (6)$$

and may be similarly stated in words.

These results may be extended to sets of n magnitudes $u_1, u_2 \ldots u_n$, each set appertaining to a member of a class which has an infinitely large membership, when $u_1, u_2 \ldots u_n$ are statistically independent Gamma variates $c(l_1),\ c(l_2)\ldots c(l_n)$. By repeated applications of (3) and (4), or (5) and (6), any r of these n variates, $r \ll n$, may be replaced in a variety of ways by r new Gamma and Beta variates statistically independent of one another and of the remaining $(n-r)$ original Gamma variates. Many of these replacements lead to results of practical importance.

III. Corresponding Normal and Gamma Variates.

The so-called " normal " frequency distribution is a theoretical continuous distribution in which the frequency density is inversely proportional to e^{kx^2}, where $x=X-A$, the deviation of the variate X from a certain value A, and k is a positive constant.

The f.d. is greatest when $x=0$; and it is the same for $-x$ as for $+x$; so A is not only the modal, but also the median, and the mean, value of X. As $|x|$ increases, the f.d. decreases, and soon becomes small ; for example, when $kx^2 =10$, it is easy to verify that the f.d. is less than $\dfrac{1}{20,000}$ of its greatest value.

Since $\displaystyle\int_{-\infty}^{\infty} e^{-k(X-A)^2}\,dX = 2\int_0^{\infty} e^{-kx^2}\,dx = \frac{\sqrt{\pi}}{\sqrt{k}}$,

the relative f.d. is $\dfrac{\sqrt{k}}{\sqrt{\pi}}e^{-kx^2}$, and the f. with which the "deviate" x has values from $-x$ to $+x$ is $2\displaystyle\int_0^{x}\frac{\sqrt{k}}{\sqrt{\pi}}e^{-kx^2}dx$.

If now we introduce a new variate u such that $u = k(X-A)^2 = kx^2$, then $dx = \dfrac{du}{2\sqrt{ku}}$, and u ranges from 0 to ∞. Hence, substituting in the above integral, the c.f. of u up to a particular value u is

$$\int_0^{u} \frac{1}{\sqrt{\pi}}e^{-u}u^{-\frac{1}{2}}du = \frac{\gamma(\frac{1}{2})}{\Gamma(\frac{1}{2})},$$

in the notation already used.

Thus any normal variate X whose f.d. is $\sqrt{\dfrac{k}{\pi}}e^{-k(X-A)^2}$ corresponds to the standard Gamma variate $u = c(\frac{1}{2})$ through the relation $u = k(X-A)^2$.

To interpret k, we note that the mean value of u is

$$\int_0^{\infty} \frac{1}{\sqrt{\pi}}e^{-u}u^{-\frac{1}{2}}u\,du = \frac{\Gamma(\frac{3}{2})}{\Gamma(\frac{1}{2})} = \tfrac{1}{2}.$$

The "variance", or square of the "standard deviation" of any variate X whose mean value is A being defined as the mean value of $(X-A)^2$, and denoted by σ^2, it follows that in the case of the above normal variate, $k\sigma^2 = \tfrac{1}{2}$. Hence the f.d. of the normal variate X with mean A and standard deviation σ may be written in the customary way as $\dfrac{1}{\sigma\sqrt{2\pi}}e^{-\frac{1}{2\sigma^2}(X-A)^2}$, and the new variate $u = \dfrac{(X-A)^2}{2\sigma^2}$ is a standard Gamma variate $c(\frac{1}{2})$.

IV. Equivalent Sets of Independent Normal and other Variates.

If $\xi_1, \xi_2 \ldots \xi_n$ are n linear functions of n given variables $x_1, x_2 \ldots x_n$, for example, $\xi_r = {}_ra_1x_1 + {}_ra_2x_2 + \ldots + {}_ra_nx_n$, it is possible to choose the coefficients a in a great variety

of ways so that $\sum_{1}^{n}\xi^2=\sum_{1}^{n}x^2.$[6] The conditions to be satisfied are of two kinds :

I, $_ra_1{}^2+{}_ra_2{}^2+\ldots+{}_ra_n{}^2=1,\ (r=1,\ 2,\ldots n)$

and II, $_ra_1\cdot{}_sa_1+{}_ra_2\cdot{}_sa_2+\ldots+{}_ra_n\cdot{}_sa_n=0\ (r\neq s).$

The following are simple instances :

$$(i)\ \xi_1=\frac{1}{\sqrt{2}}(x_1+x_2)$$

$$\xi_2=\frac{1}{\sqrt{2}}(x_1-x_2)$$

$$(ii)\ \xi_1=\frac{1}{\sqrt{13}}(2x+3y)$$

$$\xi_2=\frac{1}{\sqrt{13}}(3x-2y)$$

$$(iii)\ \xi_1=\frac{1}{\sqrt{3}}(x_1+x_2+x_3)$$

$$\xi_2=\frac{1}{\sqrt{6}}(2x_1-x_2-x_3)$$

$$\xi_3=\frac{1}{\sqrt{2}}(\qquad x_2-x_3)$$

$$(iv)\ \xi_1=\frac{1}{\sqrt{14}}(x_1+3x_2+2x_3)$$

$$\xi_2=\frac{1}{\sqrt{69}}(2x_1+4x_2-7x_3)$$

$$\xi_3=\frac{1}{\sqrt{966}}(29x_1-11x_2+2x_3).$$

In making up a set of $[\xi]$ it is easiest to make up an intermediate set $[\xi']$ with coefficients satisfying the "orthogonal" conditions II, and then to get the final set by dividing each intermediate member by the square root of the sum of the squares of its coefficients so as to satisfy the scalar conditions I. It will then be clear that in building up an intermediate set, the coefficients can be chosen quite arbitrarily for the first ξ' (except that they cannot

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[6] Carr, Mathematical Synopsis, 1880, Vol. I, Sec. 582-584.

all be 0, which would be purposeless); that all but one coefficient can be chosen at will for the second ξ' and that this one is then fixed by a single equation II; that all but two can be chosen at will for the third ξ' and that these two are then determined by two equations II; and so on. Likewise if we have already a set of r linear functions $[\xi]$ of n variables $[x]$ satisfying among themselves the conditions I and II $(r < n)$, we can find $(n - r)$ more which with the given r will form a set of n satisfying those conditions.

It is also important to note that when conditions I and II are satisfied, the value of the determinant $\triangle_a$ formed by the coefficients a is ± 1, which is easily verified in the four simple instances given above[7] [8]; and further that if the equations for $[\xi]$ in terms of $[x]$ are solved in the form $x_r = {}_rA_1\xi_1 + {}_rA_2\xi_2 + \ldots + {}_rA_n\xi_n$, the value of the determinant $\triangle_A$ formed by the coefficients A is also ± 1.

By using such a linear transformation we may replace a given set of n statistically independent normal variates $X_1 \ldots X_n$ with means $A_1 \ldots A_n$ and standard deviations $\sigma_1 \ldots \sigma_n$, by another set of n statistically independent normal variates in a great variety of ways. For, as $X_1 \ldots X_n$ are statistically independent, the f. with which X_1 has values from X_1 to $X_1 + dX_1 \ldots$ and X_n has values from X_n to $X_n + dX_n$ is

$$\frac{1}{\sigma_1\sqrt{2\pi}} e^{-\frac{1}{2\sigma_1{}^2}(X_1 - A_1)^2} dX_1 \ldots \frac{1}{\sigma_n\sqrt{2\pi}} e^{-\frac{1}{2\sigma_n{}^2}(X_n - A_n)^2} dX_n,$$

or $\dfrac{1}{(2\pi)^{\frac{n}{2}}} e^{-\frac{1}{2}(x_1{}^2 + \ldots + x_n{}^2)} dx_1 \ldots dx_n$, where $x_r = \dfrac{X_r - A_r}{\sigma_r}$,

and each x is therefore a standard normal variate with mean 0 and standard deviation 1.

Now if $[\xi]$ is any set of n linear functions of $[x]$ such that $\sum_1^n \xi^2 = \sum_1^n x^2$, we may change the variables in this compound frequency element from $[x]$ to $[\xi]$. As the Jacobian

$$\frac{\partial(x_1 \ldots x_n)}{\partial(\xi_1 \ldots \xi_n)} = \triangle_A = \pm 1$$

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[7] In (i), (ii), (iv) it will be seen that $\triangle = -1$. In such cases, by reversing the signs of the coefficients in one ξ we can have a set of $[\xi]$ such that $\triangle = +1$.

[8] Turnbull, Theory of Determinants, Matrices and Invariants, p. 155.

the element becomes, reversing the signs in one of the [ξ] if necessary,

$$\frac{1}{\sqrt{2\pi}}e^{-\frac{1}{2}\xi_1{}^2}d\xi_1 \cdot \frac{1}{\sqrt{2\pi}}e^{-\frac{1}{2}\xi_2{}^2}d\xi_2 \dots \frac{1}{\sqrt{2\pi}}e^{-\frac{1}{2}\xi_n{}^2}d\xi_n.$$

Hence the [ξ] are statistically independent, and each is a normal variate with mean 0 and standard deviation 1.

Further by substituting u_r for $\frac{1}{2}\xi_r{}^2$ we have a set of n statistically independent Gamma variates $c(\frac{1}{2})$ corresponding to the original set of n normal variates ; and these again may be replaced by various sets of n statistically independent Gamma and Beta variates as shown in Section II.

The original n independent normal variates pertaining to the class of objects O may be regarded as n units of information about the class O, and any corresponding set of normal variates forms an equivalent set of n units of information about the class O ; while any corresponding set of Gamma and Beta variates forms an equivalent set as regards the absolute values of the variates, and it will be seen later that the signs are recoverable.

V. DISTRIBUTION OF $\chi_n{}^2 = \overset{n}{\underset{1}{S}}\left(\dfrac{X_r - A_r}{\sigma_r}\right)^2$.

Replacing a set $[X]$ of n statistically independent normal variates by a corresponding set $[u]$ of n statistically independent Gamma variates $c(\frac{1}{2})$ through the relations

$u_r = \frac{1}{2}\left(\dfrac{X_r - A_r}{\sigma_r}\right)^2$, it follows, *inter alia*, by II (5) that

$\overset{n}{\underset{1}{S}}(u_r) = \overset{n}{\underset{1}{S}}\frac{1}{2}\left(\dfrac{X_r - A_r}{\sigma_r}\right)^2$ is a Gamma variate $c\left(\dfrac{n}{2}\right)$. That is to say that the cumulative frequency of values of $\overset{n}{\underset{1}{S}}\frac{1}{2}\left(\dfrac{X_r - A_r}{\sigma_r}\right)^2$ from 0 up to a particular value v is

$$\int_0^v \frac{1}{\Gamma\left(\dfrac{n}{2}\right)} e^{-v}v^{\frac{n}{2}-1}dv$$

Omitting the factor $\frac{1}{2}$, the quantity $\overset{n}{\underset{1}{S}}\left(\dfrac{X_r - A_r}{\sigma_r}\right)^2$ or the sum of the squares of n standard or " reduced " normal variates is, when these variates are statistically independent,

often denoted by χ_n^2 or simply by χ^2, and $\chi_n^2 = 2c\left(\dfrac{n}{2}\right)$.

When $n > 4$, the frequency curve $y = \dfrac{1}{\Gamma\left(\dfrac{n}{2}\right)} e^{-v} v^{\frac{n}{2}-1}$

touches the v axis at 0 as well as at ∞. With exceptions at early values of n, the frequency density is greatest at $v = \dfrac{n}{2} - 1$, and there are points of inflexion at $\sqrt{\dfrac{n}{2} - 1}$ from this maximum on either side. The mean value of v is

$$\int_0^\infty \frac{1}{\Gamma\left(\dfrac{n}{2}\right)} e^{-v} v^{\frac{n}{2}-1} v\, dv = \frac{\Gamma\left(\dfrac{n}{2}+1\right)}{\Gamma\left(\dfrac{n}{2}\right)} = \frac{n}{2}.$$

The median value, even when n is so small as 3, divides the difference between the modal and mean values roughly in the ratio $2 : 1$: so the modal, median and mean values of χ_n^2 are respectively $n - 2$, approximately $n - \dfrac{2}{3}$, and n. Thus the frequency curve is asymmetrical.

The c.f. up to any specified value of v—from which can be derived the frequency of considerable deviations from the modal value, which is what is needed in practical work—is easily computed, for the Gamma integral is readily reducible by successive integrations by parts. When n is even there are $\dfrac{n}{2}$ terms, the last of these being $\left|-e^{-v}\right|_0^v$, which is the c.f. of $c(1)$ up to the value v. When n is odd, there are $\dfrac{n-1}{2}$ terms and an additional term which is likewise the c.f. of $c(\frac{1}{2})$ up to the value v. This last is obtained by taking twice the c.f. of a standard normal variate from 0 up to the value $\sqrt{2v}$, as shown in Section III.

A table of values of $\chi_n^2 \equiv 2c\left(\dfrac{n}{2}\right)$ which are reached at selected values of the c.f. is given in a form convenient for most practical work with integral values of n up to 30 in R. A. Fisher's *Statistics for Research Workers*. For example, when $n = 20$, the c.f. of values of χ^2 from 0 to

$10 \cdot 85$ is $0 \cdot 05$; likewise the c.f. of values from $31 \cdot 41$ to ∞ is also $0 \cdot 05$: so values in regions so far as either of these is from the central values are comparatively infrequent.[9] It may, in illustration of what has been said above, be noted that the modal or *most frequent* value of χ_{20}^2 (in the sense that values within a small neighbourhood ε of this value are more frequent than within ε of any other value) is 18, the median value (corresponding to a c.f. of $0 \cdot 50$) is $19 \cdot 34$, while the mean value is 20.

It is easy to show that, just as the 1st moment m_1 of $c\left(\dfrac{n}{2}\right)$ or $\frac{1}{2}\chi_n^2$ is $\dfrac{n}{2}$, so the 2nd moment m_2 is $\dfrac{n}{2}\left(\dfrac{n}{2}+1\right)$.

Hence the standard deviation of χ_n^2 is $\sqrt{n(n+2)-n^2} = \sqrt{2n}$. Consideration of the higher moments shows that as n increases the distribution tends towards the " normal " form,[10] so that when n is large enough the frequency distribution of χ_n^2 may be regarded as that of a normal variate with mean n and standard deviation $\sqrt{2n}$. A better approximation when n is about 30 is that recommended by R. A. Fisher as a result of considering the distribution of $|\chi_n|$, which is more nearly normal. Its mean may be shown to be approximately $\sqrt{n-\frac{1}{2}}$ and its standard deviation $\dfrac{1}{\sqrt{2}}$, so $\sqrt{2\,\chi_n^2} - \sqrt{2n-1}$ may be treated as a standard normal variate.

V (a). Deficiency of Information Supplied by the χ_n^2 Distribution.

Just as it was seen in Section III that the frequency of a value of the Gamma variate $c(\frac{1}{2}) \equiv \frac{1}{2}\chi_1^2$ is made up of the frequencies of values $+x$ and $-x$ of the standard normal variate x, so it appears that the frequency of a value of $c\left(\dfrac{n}{2}\right) \equiv \frac{1}{2}\chi_n^2 = \frac{1}{2}(x_1^2 + x_2^2 + \ldots + x_n^2)$ is made up of the frequencies of the sets of values $\pm x_1, \pm x_2 \ldots \pm x_n$, and there are 2^n sets in all. Thus the variate χ_n^2 does not

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[9] The volume of elaborate *Tables of the Incomplete Gamma Function*, edited by Karl Pearson, may also be consulted.

[10] First shown by Laplace. See Todhunter's *History of Probability*, Art. 1006.

distinguish the signs of the n normal deviates to which it corresponds, and it is obviously necessary in analysing the results of an experiment to examine the signs of the deviates from the assumed or hypothetical mean or means before accepting the result of, or even applying the χ_n^2 test. As in the case of each theoretical normal variate positive and negative deviates are equally frequent, the frequency of r positive deviates among n deviates is given by $\binom{n}{r} q^{n-r} p^r$ (the general frequency in a binomial distribution) where in this case $p = q = \frac{1}{2}$.

It may happen, however, even when the signs respond satisfactorily to the binomial test, that the χ^2 test of the magnitudes of the deviates as a whole is deceptive. For example, in the case of 11 standard normal deviates x_r, suppose $\overset{10}{\underset{1}{S}}(x_r^2) = 6 \cdot 6$ and $x_{11}^2 = 8 \cdot 0$. Then $\chi_{11}^2 = \overset{11}{\underset{1}{S}}(x_r^2) = 14 \cdot 6$. This last is greater than the most frequent or modal value of χ_{11}^2, viz., 9, but R. A. Fisher's table, cited above, shows that the frequency of values greater than $14 \cdot 6$ is about $0 \cdot 20$; so the value of χ_{11}^2 derived from all the 11 observations is not of a markedly infrequent sort. On the other hand, separating χ_{10}^2 and χ_1^2, the observed value of χ_{10}^2 is certainly less than its most frequent value, viz. 8, but the frequency of values less than $6 \cdot 6$ is about $0 \cdot 25$, so this value also is not of a very uncommon kind. The value of χ_1^2, viz. $8 \cdot 0$, is, however, most unusually large. In the case of a single variate χ_1^2, the frequency of values larger than this is only $0 \cdot 0047$. As $n = 11$, the frequency with which one or more members of a set of 11 variates χ_1^2 exceed $8 \cdot 0$ is the sum of all terms but the first in the expansion of the binomial $(0 \cdot 9953 + 0 \cdot 0047)^{11}$, i.e. about $0 \cdot 05$. This result is very different from that derived above by the χ_{11}^2 test, which leads to a frequency of $0 \cdot 20$.

The deficiency, thus illustrated, of the single χ_n^2 test is accounted for in the last paragraph of Section II. The Gamma variate $c\left(\dfrac{n}{2}\right) = \frac{1}{2}\chi_n^2$ is only one of a set of n statistically independent Gamma and Beta variates corresponding to the original n normal variates. It is only one piece of information. There are also $(n-1)$ Beta variates, which may be arranged in various ways.

For example, compounding one by one the Gamma variates $u_1,\ u_2\dots u_n$ $\left[\text{where}\quad u_r=\tfrac12 x_r{}^2=\tfrac12\left(\dfrac{X_r-A_r}{\sigma_r}\right)^2\right]$, we have the following successive sets :

$$\dfrac{u_2}{u_1+u_2},\ (u_1+u_2),\ u_3\dots\dots\dots\dots\dots\dots\dots u_n\ ;$$

$$\dfrac{u_2}{u_1+u_2},\ \dfrac{u_3}{u_1+u_2+u_3},\ (u_1+u_2+u_3),\ u_4\ \dots\dots\dots u_n\ ;$$

$$\dfrac{u_2}{u_1+u_2},\ \dfrac{u_3}{u_1+u_2+u_3},\dots\dots$$

$$\dfrac{u_n}{u_1+u_2+\dots+u_n},\ (u_1+u_2+\dots+u_n).$$

The fraction $\dfrac{u_n}{u_1+u_2+\dots+u_n}$ is a Beta variate $b\left(\tfrac12,\ \dfrac{n-1}{2}\right)$. Its c.f. up to the value θ is

$$\int_0^\theta \frac{\Gamma\!\left(\dfrac{n}{2}\right)}{\Gamma(\tfrac12)\Gamma\!\left(\dfrac{n-1}{2}\right)}\theta^{\frac12-1}(1-\theta)^{\frac{n-1}{2}-1}d\theta$$

When $n>3$ (the cases $n=2$ and 3 being mainly of theoretical interest), the frequency curve $y=K\theta^{-\frac12}(1-\theta)^{\frac{n-3}{2}}$ is J-shaped, the y axis being an asymptote. As in the case of the Gamma variate $c(\tfrac12)$, values of θ within a small neighbourhood ε of zero are more frequent than within ε of any other value. The mean value of θ (which in the case of J-shaped distributions is a good measure of dispersion) is

$$\frac{\Gamma\!\left(\dfrac{n}{2}\right)}{\Gamma(\tfrac12)\Gamma\!\left(\dfrac{n-1}{2}\right)}\cdot\frac{\Gamma\!\left(\dfrac32\right)\Gamma\!\left(\dfrac{n-1}{2}\right)}{\Gamma\!\left(\dfrac{n+2}{2}\right)}=\frac1n.$$

In the above numerical case $n=11$, $\theta=\dfrac{8\cdot0}{14\cdot6}=0\cdot548$, or about 6 times the mean value. As n is odd, the c.f. up to $0\cdot548$ is easily evaluated by expanding $(1-\theta)^4$ and integrating the separate terms of the integrand. But tables of the c.f. of the Beta variate $b(p,q)$ are now available for those values of p and q which are likely to occur in current statistical analysis.[11] Noting that the c.f. from

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[11] Pearson's Tables of the Incomplete Beta Function.

0 to θ of $b(p, q)=1$—the c.f. of $b(q, p)$ from 0 to $1-\theta$ and entering these tables for $q=\frac{1}{2}$, $p=5$, with the argument $1-0\cdot548$, the frequency with which $\dfrac{u_n}{u_1+u_2+\ldots+u_n}$ exceeds $0\cdot548$ is found to be $0\cdot006$.

This, however, is the frequency with which the ratio of a particular one of a set of n Gamma variates $c(\frac{1}{2})$ to their sum exceeds $0\cdot548$. If it is desired to find the frequency with which some one, some two, and so on, and hence at least one of the ratios $\dfrac{u_1}{S(u)}$, $\dfrac{u_2}{S(u)}$, $\ldots\dfrac{u_n}{S(u)}$ exceeds a particular value, it is not possible to use a binomial distribution as in the earlier discussion of this numerical example, because, while each $\dfrac{u_r}{S(u)}$ is statistically independent of $S(u)$, these ratios are not statistically independent of one another as their sum is 1. However, it is possible to say as regards the 11 Gamma variates $c(\frac{1}{2})$, that the mean number of individuals in such sets of 11 whose ratio to the sum of the members of the set exceeds $0\cdot548$ is $0\cdot006\times11=0\cdot07$ approx.; and this provides a fairly satisfactory measure of the comparative infrequency of such an occurrence. In this particular case, however, as $0\cdot548>0\cdot5$ and therefore not more than one of the ratios can exceed $0\cdot548$, the frequency with which some one of the ratios exceeds $0\cdot548$ is also $0\cdot006\times11=0\cdot07$ approx.

Summarising these results, it appears that in order to have the same body of information as is available in the two statistically independent variates χ_{n-1}^2 and χ_1^2, it is necessary to consider both the statistically independent variates χ_n^2 and $\dfrac{\chi_1^2}{\chi_n^2}$, which are equivalent to the former two.

Likewise, in the foregoing numerical example, the χ_{10}^2 test may also be deceptive, and so it may be necessary to separate χ_{10}^2 into two independent portions χ_9^2 and another χ_1^2 and examine both these. Equivalently in the corresponding set of 10 Beta variates and one Gamma variate $\frac{1}{2}\chi_{11}^2$, and generally, it will be necessary also to examine the penultimate Beta variate

$$\dfrac{u_{n-1}}{u_1+u_2+\ldots+u_{n-1}}$$

and so on, until all the $(n-1)$ Beta variates have been

examined as well as the single Gamma variate $\frac{1}{2}\chi_n^2$—if it is desired to have the same body of information as is available in the n separate variates $\frac{1}{2}\chi_1^2$. ✓

V (b). STUDENT'S t DISTRIBUTION.

Returning to the c.f. up to the value θ of the Beta variate $\dfrac{u_n}{u_1+u_2+\ldots+u_n}=b\left(\frac{1}{2},\ \frac{n-1}{2}\right)$, which is

$$\int_0^\theta \frac{\Gamma\left(\dfrac{n}{2}\right)}{\Gamma(\frac{1}{2})\Gamma\left(\dfrac{n-1}{2}\right)}\,\theta^{-\frac{1}{2}}(1-\theta)^{\frac{n-3}{2}}d\theta,$$

we may make the substitution $\dfrac{\theta}{1-\theta}=w^2$ so that

$\dfrac{u_n}{u_1+u_2+\ldots+u_{n-1}}=w^2$. The range of w^2 is from 0 to ∞ and we may assign to w, whose range is from $-\infty$ to $+\infty$, the same sign as x_n, the standard normal variate to which u_n corresponds.

With this substitution the above c.f. becomes

$$\int_{-w}^{w}\frac{\Gamma\left(\dfrac{n}{2}\right)}{\Gamma(\frac{1}{2})\Gamma\left(\dfrac{n-1}{2}\right)}\,\frac{dw}{(1+w^2)^{\frac{n}{2}}}$$

Student's t integral is a variant of this well known integral found by putting $w^2=\dfrac{t^2}{n-1}$, so that $t^2=$

$$\dfrac{u_n}{\dfrac{1}{n-1}(u_1+u_2+\ldots+u_{n-1})}$$

Thus t^2 is the ratio of one Gamma variate $c(\frac{1}{2})$ to the average of $(n-1)$ Gamma variates $c(\frac{1}{2})$, all these variates being statistically independent. Writing ν for $n-1$, which is the number of variates in the denominator of t^2, the c.f. of values of t from $-\infty$ to any specified t is

$$\int_{-\infty}^{t}\frac{\Gamma\left(\dfrac{\nu+1}{2}\right)}{\sqrt{\pi\nu}\,\Gamma\left(\dfrac{\nu}{2}\right)}\,\frac{dt}{\left(1+\dfrac{t^2}{\nu}\right)^{\frac{\nu+1}{2}}}$$

which is Student's form.

A condensed table of this c.f. as computed by "Student" for values of t at intervals of $0 \cdot 1$ may be found in Yule and Kendall's *Theory of Statistics*, 1937, and an inverted table of values of t which correspond to selected values of the c.f., in R. A. Fisher's *Statistics for Research Workers*.

As $t^2 = (n-1)w^2 = (n-1)\dfrac{\theta}{1-\theta}$, we have $\theta = \dfrac{t^2}{n-1+t^2}$, and therefore the c.f. of values of t from 0 to any particular value t may be found independently of Student's table by taking half the c.f. of values of θ up to $\dfrac{t^2}{n-1+t^2}$ from Pearson's *Tables of the Incomplete Beta Function* $\left(\dfrac{1}{2}, \dfrac{n-1}{2}\right)$. To verify by Student's table the result thus obtained from the numerical example treated above, viz. $\frac{1}{2}(0 \cdot 006)$, we have

$$t^2 = (n-1)\frac{\theta}{1-\theta} = 10 \times \frac{0 \cdot 548}{0 \cdot 452} = 12 \cdot 1 \; ; \quad t = \pm 3 \cdot 48$$

according to the sign of x_n, the standard variate to which u_n corresponds ; and Student's table gives $0 \cdot 003$ for the frequency of values of t exceeding $3 \cdot 48$ (or less than $-3 \cdot 48$).

It is worth noting that, writing Student's integral briefly as $\displaystyle\int_{-w}^{w} K \frac{dw}{(1+w^2)^{\frac{n}{2}}}$, the mean value of w^2 is

$$\int_{-\infty}^{\infty} K \left\{ \frac{1+w^2}{(1+w^2)^{\frac{n}{4}}} - \frac{1}{(1+w^2)^{\frac{n}{2}}} \right\} dw$$

$$= \frac{\Gamma\left(\frac{n}{2}\right)\Gamma\left(\frac{n-3}{2}\right)}{\Gamma\left(\frac{n-1}{2}\right)\Gamma\left(\frac{n-2}{2}\right)} - 1 = \frac{1}{n-3}$$

So the standard deviation of w is $\dfrac{1}{\sqrt{n-3}}$ and as $t = w\sqrt{n-1}$ the s.d. of t is $\sqrt{\dfrac{n-1}{n-3}} = \sqrt{\dfrac{\nu}{\nu-2}}$. Even for quite moderate values of ν, a close approximation for frequencies important in practical work is obtained by treating t as a normal variate about mean zero with this standard devia-

tion. For example if $\nu=6$, the s.d. is $\sqrt{\dfrac{6}{4}}=1\cdot225$. Student's table gives $0\cdot475$ as the frequency with which t is between 0 and $+2\cdot447$. The corresponding frequency in the normal distribution of values of x between 0 and $\dfrac{+2\cdot447}{1\cdot225}=+2$ nearly, is $0\cdot477$. This method of approximation is useful when the elaborate tables are not available.

VI. DISTRIBUTION OF $\chi_{n-1}{}^2=\overset{n}{\underset{1}{S}}\left(\dfrac{X-X}{\sigma}\right)^2$, AND OF STUDENT'S ORIGINAL t.

When the n statistically independent variates X_1, $X_2\ldots X_n$ are members of identical normal distributions (each having mean A and standard deviation σ), a Gamma variate can be derived which does not involve the mean A, and a Beta variate can be derived which also is a symmetrical function of the n variates and does not involve the standard deviation σ. The corresponding standard normal variates being x_1, $x_2\ldots x_n$ where $x_r=\dfrac{X_r-A}{\sigma}$, we may take any orthogonal set $[\xi]$, as described in Section IV, in which

$$\xi_1=\frac{1}{\sqrt{n}}(x_1+x_2+\ldots+x_n)=\sqrt{n}\,.\,\bar{x}$$

Then

$$\tfrac{1}{2}n\left(\frac{X-A}{\sigma}\right)^2=\tfrac{1}{2}n\bar{x}^2=\tfrac{1}{2}\xi_1{}^2=u_1$$

Further

$$\overset{n}{\underset{1}{S}}\left(\frac{X_r-\bar{X}}{\sigma}\right)^2=\overset{n}{\underset{1}{S}}(x_r-\bar{x})^2=\overset{n}{\underset{1}{S}}x_r{}^2-n\bar{x}^2$$

Hence

$$\tfrac{1}{2}\overset{n}{\underset{1}{S}}\left(\frac{X_r-\bar{X}}{\sigma}\right)^2=\overset{n}{\underset{1}{S}}\tfrac{1}{2}\xi_r{}^2-\tfrac{1}{2}\xi_1{}^2=\overset{n}{\underset{2}{S}}u_r$$

As the n Gamma variates $[u]$ are statistically independent, it follows (a) that $\tfrac{1}{2}\overset{n}{\underset{1}{S}}\left(\dfrac{X_r-\bar{X}}{\sigma}\right)^2$ is a Gamma variate $c\left(\dfrac{n-1}{2}\right)=\tfrac{1}{2}\chi_{n-1}{}^2$; (b) that, omitting the common factor $\dfrac{1}{2\sigma^2}$, $\dfrac{n(\bar{X}-A)^2}{n(\bar{X}-A)^2+\overset{n}{\underset{1}{S}}(X_r-\bar{X})^2}$ is a Beta variate $b\left(\tfrac{1}{2},\ \dfrac{n-1}{2}\right)$.

As in Section V (b), we may read directly in "Tables of the Incomplete Beta Function" the c.f. of values of this ratio from 0 to any specified value θ, or the c.f. of values of

$$\frac{n(\overline{\overline{X}}-A)^2}{\overset{n}{\underset{1}{S}}(X_r-\bar{X})^2}$$ up to any specified value w^2, or the c.f. of values

of $$\frac{n(\overline{\overline{X}}-A)^2}{\dfrac{1}{n-1}\overset{n}{\underset{1}{S}}(X_r-\bar{X})^2}$$ up to any specified value t^2 by entering

the Beta table with the arguments θ, $\dfrac{w^2}{1+w^2}$ and $\dfrac{t^2}{n-1+t^2}$ respectively.

Alternatively, as in Section V (b), we may use Student's table to find the c.f. of values of the square root of the last of these ratios, viz. $$\frac{\overline{X}-A}{\sqrt{\dfrac{1}{n(n-1)}\overset{n}{\underset{1}{S}}(X-\bar{X})^2}},$$ from 0 to the

specified value t_ν, where, as before, $\nu = n-1$, the number of statistically independent variates entering the denominator; and this result is necessarily a half, as before, of the c.f. of values of the ratio itself up to the specified value t^2 as read from the Beta tables.

Illustration of Use of χ_{n-1}^2.

Taking the eleven observations $5\cdot0$, $4\cdot8$, $5\cdot0$, $5\cdot4$, $4\cdot5$, $5\cdot6$, $5\cdot8$, $3\cdot9$, $6\cdot3$, $6\cdot5$, $2\cdot2$, the hypothesis being that these are values of statistically independent variates in identical normal distributions, whose common mean A and variance σ exist but are unknown, we have $\overline{X}=5\cdot0$, $\overset{11}{\underset{1}{S}}(X-\bar{X})^2 = 14\cdot4$; thus $\dfrac{14\cdot4}{\sigma^2}$ is a value of χ_{10}^2. As this is an instance of one of the most important practical problems of statistics, it is necessary to take care with the reasoning. If the only information with regard to the variance σ^2 is what can be surmised from these 11 observations, we may note (1) that the most frequent value of χ_{10}^2 is 8, and that the frequencies of other values, all being forced say to one place of decimals, form two diminishing sequences; (2) that χ_{10}^2 is as often less than as greater than about 9¼, its median value, and (3) that the mean of all values of χ_{10}^2 is 10. The value that we find for σ^2 depends on the value which we assume to be taken by

χ_{10}^2 as a result of the normal variates taking just these 11 values. If we assume that it is the most frequent value of χ_{10}^2, then we find $\sigma^2 = 1 \cdot 8$, if the mean value of χ_{10}^2, then $\sigma^2 = 1 \cdot 44$, if the median value, then $\sigma^2 = 1 \cdot 5$. If it is asked what is the best estimate of σ^2, the answer is that in order to make a decision, it is necessary to beg some more or less acceptable principle which attaches a special meaning to the word " best ".

Whatever single estimate may be regarded as the " best ", we may still note, *inter alia*, that the frequency of values of χ_{10}^2 less than about 4 is $0 \cdot 05$, and of values greater than about 18 is also $0 \cdot 05$. Hence we might expect to be wrong on an average once in ten trials if we adopted the procedure of dividing by 4 and 18 respectively, and regarding the variance as lying between the resulting quotients, which, in the case of these particular eleven observations, are $3 \cdot 6$ and $0 \cdot 8$. Correspondingly, the standard deviation σ would be estimated as lying between about $1 \cdot 9$ and $0 \cdot 9$. This is a rather wide bracket.

Suppose, however, we have 31 instead of 11 observations, showing about the same average dispersion from their mean, so that $\overset{31}{\underset{1}{S}}(X - \bar{X})^2 = 43$ say ; then, noting that the f. either of values of χ_{30}^2 less than $18 \cdot 5$, or of values greater than about 44 is $0 \cdot 05$, we have a corresponding bracket of $2 \cdot 3$ down to $1 \cdot 0$ for the variance, and of $1 \cdot 5$ to $1 \cdot 0$ for the standard deviation σ. Thus the increase in the number of components of χ^2 from 10 to 30 has reduced the width of the standard deviation bracket by about one-half.

What is needed in practice, however, is an estimate of the standard deviation of $\bar{X}$ from the mean A. In the case of the 11 observations this is $\dfrac{\sigma}{\sqrt{11}}$, and the bracket for the s.d. of $\bar{X}$ is therefore $0 \cdot 57$ to $0 \cdot 27$; while in the case of the 31 observations the s.d. of $\bar{X}$ is $\dfrac{\sigma}{\sqrt{31}}$ and the bracket is $0 \cdot 27$ to $0 \cdot 18$. In both cases there is marked reduction in the width of the original brackets and in the size of the limits, but the reduction in the second case is $\sqrt{\dfrac{31}{11}}$ times that in the first case, so that on the whole the width of the final bracket for the s.d. of the mean of 31 observations is less than one-third of that for the s.d. of the mean of 11 observations.

Taking the case of the 11 observations for an example of a final inference, and noting that $0 \cdot 05$ is the frequency with which a normal variate takes values differing from its mean by more than twice (more exactly $1 \cdot 96$ times) its standard deviation, we conclude that the mean $\overline{X}$ of the 11 observations differs from the mean A with a frequency of $0 \cdot 05$ by more than some quantity which, we estimate, lies between about $0 \cdot 5$ and $1 \cdot 1$, with the reservation that the procedure we have adopted may be expected to lead us astray in the long run in about 10% of cases.

Illustration of Use of $\dfrac{\overline{X} - A}{\sqrt{\dfrac{1}{n(n-1)} \overset{n}{\underset{1}{S}}(X - \overline{X})^2}}$ = **Student's Original t.**

While the use of χ_{n-1}^2, illustrated above, to assess the standard deviation or scale of the identical normal distributions to which the eleven variates belong stands good, the method, illustrated in the last two paragraphs, of using that estimated scale to locate the common mean A has been superseded by the use of Student's variate. This permits a more compendious kind of inference.

In the case of 11 observations the number, ν, of statistically independent Gamma variates $c(\frac{1}{2})$ or $\frac{1}{2}\chi_1^2$ entering the denominator of t is 10. With this value of ν Student's table of t shows that $|t|$ exceeds $2 \cdot 23$ with frequency $0 \cdot 05$. [This figure can be verified in Pearson's tables of $b\left(\frac{1}{2}, \dfrac{\nu}{2}\right)$, which show that $b(\frac{1}{2}, 5)$ exceeds $0 \cdot 332$ with frequency $0 \cdot 05$. As $|t| = \sqrt{\dfrac{\nu\theta}{1-\theta}}$ where θ is the corresponding value of $b(\frac{1}{2}, 5)$, we have $|t| = \sqrt{\dfrac{3 \cdot 32}{0 \cdot 668}} = 2 \cdot 23$].

For these 11 observations the resulting value of t is $\dfrac{5-A}{\sqrt{\dfrac{14 \cdot 4}{11 \times 10}}} = \dfrac{5-A}{0 \cdot 36}$. We do not know the value of A, and therefore we do not know the actual value of t that has arisen from the 11 observations. But we do know that values of t within a small neighbourhood ε of zero are more frequent than within ε of any other value; that, if t_1 is positive, values of t within ε of $+t_1$ are as frequent as values of t within ε of $-t_1$; that corresponding to any sequence of increasing positive numbers t_1, t_2, $t_3 \cdots$

we have two diminishing sequences of frequencies ; that t takes values between $-2 \cdot 23$ and $+2 \cdot 23$ with frequency $0 \cdot 95$, and beyond these values with frequency $0 \cdot 05$; that t takes values between $-3 \cdot 17$ and $+3 \cdot 17$ with frequency $0 \cdot 99$, and beyond these values with frequency $0 \cdot 01$, and so on. If the confidence with which we assign a range of values for A varies directly with the frequency of the resulting range of values of t, then we have more confidence in assigning for A the range $5 \mp \delta$ than the range $5 + 0 \cdot 36 t \mp \delta$ where t is any number not zero, and $\mp \delta$ defines a small neighbourhood. Further, we have 19 times as much confidence in locating A between $5 \mp 0 \cdot 36 \times 2 \cdot 23$, i.e. $4 \cdot 2$ to $5 \cdot 8$, as in locating it beyond these values, and at the same time we have more confidence in locating A within $+ \delta$ of any value within this range than within $\mp \delta$ of any value beyond this range.

If such confidence is not sufficient and we take a more extended range, e.g. $5 \mp 0 \cdot 36 \times 3 \cdot 17$, i.e. $3 \cdot 86$ to $6 \cdot 14$, we have 99 times as much confidence in locating A between these two values as beyond them, while retaining as before our confidence in every particular value within this range as against every particular value beyond it. If this last condition is satisfied, the range corresponding to any confidence ratio is determined uniquely ; for if we shift the range so found ever so little while maintaining the ratio, we thereby include within the range a value in which we have less confidence than in a value which we leave outside it. This condition is applicable also when there is only one diminishing sequence of frequencies, as in the case of the distribution of $c(\frac{1}{2})$ or that of t^2. It effectually excludes the use of the cumulative frequency to infer " significance " in the case of a " rectangular " distribution (of constant frequency density), which is as it should be.

As noted above, a good approximation to the distribution of t in some important regions is found by treating

$$\frac{\bar{X} - A}{\sqrt{\dfrac{1}{n(n-3)} \overset{n}{\underset{1}{S}} (X - \bar{X})^2}}$$

as a standard normal variate (with mean 0 and s.d. 1). This amounts to estimating the variance as $\dfrac{1}{n-3} \overset{n}{\underset{1}{S}} (X - \bar{X})^2$ rather than $\dfrac{1}{n-1} \overset{n}{\underset{1}{S}} (X - \bar{X})^2$, which is justifiable if we regard the values of $\dfrac{S(X - \bar{X})^2}{\_^2}$ as centralised at the most

frequent rather than the mean value of χ_{n-1}^2; the corresponding estimate of the variance of $\bar{X}$ is then

$$\frac{1}{n(n-3)}\overset{n}{\underset{1}{S}}(X-\bar{X})^2$$

In the present numerical example, the denominator is $\sqrt{\dfrac{14\cdot4}{11\times8}}=0\cdot405$; hence the frequency with which $\dfrac{|\bar{X}-A|}{0\cdot405}$ exceeds $1\cdot96$, or $|\bar{X}-A|$ exceeds $0\cdot79$, is $0\cdot05$. This is comparable with $0\cdot80$ as derived from the t table. For narrower and wider confidence ranges the agreement is not quite so good. For example, for the frequency $0\cdot01$ we find $|\bar{X}-A|>1\cdot14$ by the t table as against $1\cdot04$ by the standard normal table. For many (but not all) practical purposes, however, these discrepancies are not important.

VII. Deficiency of Information Supplied by the χ_{n-1}^2 and t_{n-1} Distributions. Further t Variates.

The two distributions just considered, although not statistically independent, contain an important part, but not the whole, of the information inherent in the n variates $X_1, X_2 \ldots X_n$. In compounding the $(n-1)$ Gamma variates $\frac{1}{2}\xi_2^2, \frac{1}{2}\xi_3^2 \ldots \frac{1}{2}\xi_n^2$ to form the single Gamma variate $c\left(\dfrac{n-1}{2}\right)$ or $\frac{1}{2}\chi_{n-1}^2$ no account was taken of the $(n-2)$ Beta variates which with that Gamma variate form a set of $(n-1)$ variates equivalent to $[\xi_2, \xi_3 \ldots \xi_n]$. For the purpose of deriving χ_{n-1}^2 it was not necessary to do more than specify ξ_1 in terms of the members of the set $[X]$. To recover the rest of the information we will choose $\xi_2 \ldots \xi_n$ as follows, rewriting ξ_1 to complete the set $[\xi]$:

$$\xi_1 = \frac{1}{\sqrt{n}}(x_1 + x_2 + x_3 + \ldots \qquad\qquad + x_n)$$

$$\xi_2 = \frac{1}{\sqrt{n(n-1)}}(-\overline{n-1}\,x_1 + x_2 + x_3 + \ldots \qquad + x_n)$$

$$\xi_3 = \frac{1}{\sqrt{(n-1)(n-2)}}(-\overline{n-2}\,x_2 + x_3 + \ldots \qquad + x_n)$$

$$\xi_n = \frac{1}{\sqrt{2}}(\qquad\qquad\qquad\qquad\qquad -x_{n-1} + x_n)$$

One complete set of statistically independent Gamma and Beta variates replacing the set $[\xi]$ is :

(1) $\frac{1}{2}\underset{1}{\overset{n}{S}}\xi^2 = \frac{1}{2}\chi_n{}^2 = c\left(\dfrac{n}{2}\right)$

(2) $\dfrac{\xi_1{}^2}{\underset{1}{\overset{n}{S}}\xi^2} = b\left(\tfrac{1}{2},\ \dfrac{n-1}{2}\right)$

(3) $\dfrac{\xi_2{}^2}{\underset{2}{\overset{n}{S}}\xi^2} = b\left(\tfrac{1}{2},\ \dfrac{n-2}{2}\right)$

(4) $\dfrac{\xi_3{}^2}{\underset{3}{\overset{n}{S}}\xi^2} = b\left(\tfrac{1}{2},\ \dfrac{n-3}{2}\right)$, and so on.

It has been shown above that (2) may be replaced by a t_ν variate, where $\nu = n-1$. Similarly it can be shown that (3) may be replaced by a t_ν variate, where $\nu = n-2$, viz.

$$\dfrac{\xi_2}{\sqrt{\dfrac{1}{n-2}\underset{3}{\overset{n}{S}}\xi^2}}$$

We then have

$$\xi_2 = \sqrt{\dfrac{n}{n-1}}(-x_1 + \bar{x}) = \sqrt{\dfrac{n}{n-1}}\left(\dfrac{-X_1 + X}{\sigma}\right)$$

$$\underset{3}{\overset{n}{S}}\xi^2 = \underset{1}{\overset{n}{S}}x^2 - n\bar{x}^2 - \dfrac{n}{n-1}(-x_1 + \bar{x})^2$$

$$= \underset{1}{\overset{n}{S}}\left(\dfrac{X - \bar{X}}{\sigma}\right)^2 - \dfrac{n}{n-1}\left(\dfrac{-X_1 + \bar{X}}{\sigma}\right)^2$$

Hence $\dfrac{\sqrt{\dfrac{n}{n-1}}(-X_1 + \bar{X})}{\sqrt{\dfrac{1}{n-2}\left\{\underset{1}{\overset{n}{S}}(X - \bar{X})^2 - \dfrac{n}{n-1}(-X + \bar{X})^2\right\}}}$ is a t_ν variate,

where $\nu = n-2$, and this variate involves neither the mean A nor the standard deviation σ.

Among the 11 observations examined above there is one observation $2 \cdot 2$. Putting $X_1 = 2 \cdot 2$, $X = 5 \cdot 0$, $\underset{1}{\overset{n}{S}}(X - \bar{X})^2 = 14 \cdot 4$, we have, as an observed value of t_{n-2},

$$\dfrac{\sqrt{\dfrac{11}{10}} \times 2 \cdot 8}{\sqrt{\dfrac{1}{9}\left\{14 \cdot 4 - \dfrac{11}{10}(2 \cdot 8)^2\right\}}} = 3 \cdot 65.$$

The t table shows that $|t_9|$ exceeds this value with frequency $0 \cdot 0052$. This is the frequency with which a particular one of the set $[X]$ provides such a value of t. As the values of t provided by the 11 members of the set are not statistically independent, since $\overset{n}{\underset{1}{S}}\left(\dfrac{t^2}{n-2+t^2}\right)=\dfrac{n}{n-1}=1\cdot 1$, it is not easy to state the frequency with which some one, some two, etc., provide values of t exceeding some specified value. We may, however, say that among sets of 11, the mean number of members of a set which provide values of the above t_9 variate exceeding $3\cdot 65$ in absolute value is $0\cdot 0052\times 11$ or $0\cdot 06$ approximately.

Thus we might expect such a value of t_9 in the case of only one member of one set of eleven on an average among 17 such sets, and in some experimental circumstances we might feel justified in rejecting the hypothesis of "n identical normal distributions" as regards this variate.

The same result is obtained more clearly by using, as already illustrated, the Beta variate

$$b\left(\tfrac{1}{2},\ \frac{n-2}{2}\right)=\frac{\dfrac{n}{n-1}(-X_1+\bar{X})^2}{\overset{n}{\underset{1}{S}}(X-\bar{X})^2}$$

The value taken in this case is $0\cdot 599$, and Pearson's table for $b(4\tfrac{1}{2},\ \tfrac{1}{2})$, entered with the argument $1-0\cdot 599$, gives $0\cdot 0052$ as the frequency with which this value is exceeded. Thus in this numerical example the frequency with which the ratio of a particular one of the eleven quantities $(X_r-\bar{X})^2$ to their sum exceeds $\dfrac{10}{11}(0\cdot 599)$ or $0\cdot 545$ is $0\cdot 0052$ and therefore, as not more than one such ratio in the set of eleven can exceed $0\cdot 545$, the frequency with which some one exceeds $0\cdot 545$ is $0\cdot 0052\times 11=0\cdot 06$ approx.

It is important to note that (1), Student's original t_{n-1} variate, (2) this last t_{n-2} variate, and (3) the Gamma variate

$$c\left(\frac{n}{2}\right)=\tfrac{1}{2}\chi_n^2=\tfrac{1}{2}\overset{n}{\underset{1}{S}}(\xi_r^2)=\tfrac{1}{2}\overset{n}{\underset{1}{S}}(x^2)=\tfrac{1}{2}\overset{n}{\underset{1}{S}}\left(\frac{X-A}{\sigma}\right)^2$$

are statistically independent of one another; that is to say, *inter alia*, that the frequency with which t_{n-2} takes any of its values is independent of the value taken by t_{n-1}, and, by (3), is the frequency in all possible sets $[X_1,\ X_2\ldots .X_n]$ of variates in the n identical normal distributions with mean A and s.d. σ.

It may likewise be shown that the above Beta variate (4), viz. $\dfrac{\xi_3^2}{\underset{3}{\overset{n}{S}}\xi^2}$, may be replaced by a further statistically

independent t_{n-3} variate $\dfrac{\xi_3}{\sqrt{\dfrac{1}{n-3}\underset{4}{\overset{n}{S}}\xi^2}}$, which like t_{n-2} involves

neither the common mean A nor the variance σ^2 of the variates (X), and is

$$\dfrac{\sqrt{\dfrac{n-1}{n-2}}(-X_2+{}_1\bar{X})}{\sqrt{\dfrac{1}{n-3}\left\{\underset{1}{\overset{n}{S}}(X-\bar{X})^2-\dfrac{n}{n-1}(-X_1+\bar{X})^2-\dfrac{n-1}{n-2}(-X_2+{}_1X)^2\right\}}}$$

where ${}_1\bar{X}$ denotes $\dfrac{1}{n-1}\underset{2}{\overset{n}{S}}X_r$. Continuing this process we

have χ_n^2, t_{n-1}, t_{n-2}, t_{n-3} .... t_1 as a set of n statistically independent variates equivalent to the n variates $[X]$.

This is only one of the many alternative equivalent sets which may be derived from the set $[\xi]$; further, the set $[\xi]$ chosen here is but one of many sets which may be used to replace the set $[x]$: so equivalent sets of n statistically independent $[c, b]$ or $[\chi^2, t]$ variates can be chosen to replace the original set $[X]$ in a great variety of ways. In testing observations there is some advantage in using variates from the same set; variates taken from different sets are not necessarily statistically independent and inferences may not be so easily drawn.

It is worth noting that the above t_{n-2} variate may be deduced directly from the set $[x]$ without interposing the set $[\xi]$. For if ${}_1\bar{x}$ denotes $\dfrac{1}{n-1}\underset{2}{\overset{n}{S}}x_r$, then $\underset{2}{\overset{n}{S}}(x_r-{}_1\bar{x})^2$ is statistically independent of ${}_1\bar{x}$ and therefore of $-x_1+{}_1x$ whose variance is $\dfrac{n}{n-1}$. Then

$$2c(\tfrac{1}{2})=\dfrac{n-1}{n}(-x_1+{}_1x)^2=\dfrac{n}{n-1}(-x_1+\bar{x})^2$$

Also

$$2c\left(\dfrac{n-2}{2}\right)=\underset{2}{\overset{n}{S}}(x_r-{}_1\bar{x})^2=\underset{2}{\overset{n}{S}}(x_r-\bar{x})^2-(n-1)(\bar{x}-{}_1\bar{x})^2$$

$$=\underset{1}{\overset{n}{S}}(x_r-\bar{x})^2-\dfrac{n}{n-1}(-x_1+\bar{x})^2$$

Hence

$$b\left(\tfrac{1}{2},\ \frac{n-2}{2}\right) = \frac{c(\tfrac{1}{2})}{c(\tfrac{1}{2})+c\left(\dfrac{n-2}{2}\right)} = \frac{\dfrac{n}{n-1}(-x_1+\bar{x})^2}{\overset{n}{\underset{1}{S}}(x_r-\bar{x})^2}$$

$$= \frac{\dfrac{n}{n-1}(-X_1+\bar{X})^2}{\overset{n}{\underset{1}{S}}(X_r-\bar{X})^2}$$

and the t_{n-2} variate follows as above. While this method may be used to verify the remaining t variates, it does not establish the statistical independence of the members of the new set or that the new set is equivalent to the original set $[X]$.

VIII. Fisher's z Distribution.

A set of n statistically independent normal variates $[X]$ pertaining to a member of a class of objects O may be divided into sets of n_1 and n_2 where $n=n_1+n_2$. The set of n_1 may be replaced by $\sqrt{n_1}.\bar{x}_1$, $\chi_{n_1-1}^2$, t_{n_1-2}, $t_{n_1-3}\cdots t_1$, and the set of n_2 likewise by $\sqrt{n_2}.\bar{x}_2$, χ_{n_2-1}, and (n_2-2) successively derived t variates, stopping short, in each case, of Student's t_{n-1} variate $\dfrac{\sqrt{n}.\bar{x}}{\sqrt{\dfrac{1}{n-1}\chi_{n-1}^2}}$. If the variates $[X]$ have in common the mean A and variance σ^2, the new set of n statistically independent variates is

$$\sqrt{n_1}\frac{\bar{X}_1-A}{\sigma},\ \frac{S_1(X-\bar{X}_1)^2}{\sigma^2}\ \text{and}\ (n_1-2)\ \text{variates}\ t,$$

$$\sqrt{n_2}\frac{\bar{X}_2-A}{\sigma},\ \frac{S_2(X-\bar{X}_2)^2}{\sigma^2}\ \text{and}\ (n_2-2)\ \text{variates}\ t,$$

and none of these t variates involves either A or σ. Hence may be devised various tests of the consistency of n observations with the hypothesis of normal distribution with common mean and variance. We may examine the various t variates as in the preceding example. We may also examine the ratio of the two variates $\dfrac{1}{\sigma^2}S_1$ and $\dfrac{1}{\sigma^2}S_2$ or $S_1:S_2$, which is the " z test " devised by R. A. Fisher. This ratio also involves neither A nor σ. Advantage of this fact may be taken in numerical computations. We

may add to (or subtract from) each of the n observations any positive number, and then multiply (or divide) each result by any positive number, without affecting the observed values of these t variates ($t_1 \ldots t_{n-2}$) or of $S_1 : S_2$. In short, these variates are independent of the " location " and " scale " of the common normal distribution of $[X]$. They may be regarded as invariant sampling distributions for the whole family of normal distributions.

As $\dfrac{S_1}{\sigma^2} = \chi_{n_1-1}{}^2 = 2c\left(\dfrac{n_1-1}{2}\right) \; ; \quad \dfrac{S_2}{\sigma^2} = \chi_{n_2-1}{}^2 = 2c\left(\dfrac{n_2-1}{2}\right)$

it follows from Section II, writing ν for $n-1$, that $\dfrac{S_1}{S_1+S_2}$

is a Beta variate $b\left(\dfrac{\nu_1}{2}, \dfrac{\nu_2}{2}\right)$, whose c.f. from 0 to a particular value θ is

$$\frac{\Gamma\left(\dfrac{\nu_1+\nu_2}{2}\right)}{\Gamma\left(\dfrac{\nu_1}{2}\right)\Gamma\left(\dfrac{\nu_2}{2}\right)} \int_0^\theta \theta^{\frac{\nu_1}{2}-1}(1-\theta)^{\frac{\nu_2}{2}-1} d\theta$$

The Beta integral, both complete and incomplete, is an old integral in the history of the theory of probability, particularly in connection with probabilities of hypotheses as developed by Bayes and Laplace. Laplace developed ingenious methods of estimating the frequency of considerable deviations from the most frequent or modal value.[12]

The variate θ takes values from 0 to 1. Substitution of φ for $1-\theta$ shows that the frequency of values of $b\left(\dfrac{\nu_1}{2}, \dfrac{\nu_2}{2}\right)$ from 0 to α is the same as the frequency of values of $b\left(\dfrac{\nu_2}{2}, \dfrac{\nu_1}{2}\right)$ from $1-\alpha$ to 1 ; so a table of the c.f. for a series of values from 0 to 1 of one of these variates will suffice for both.

The case when $\nu_1 = 1$ has been dealt with already in reference to the t variates, but without special note of the particular case when also $\nu_2 = 1$, which will be referred to later. When both ν_1 and $\nu_2 > 2$, the f.d. of $\theta = b\left(\dfrac{\nu_1}{2}, \dfrac{\nu_2}{2}\right)$

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[12] Todhunter's History, (op. cit.), Art. 957 et passim, also Uspensky (op. cit.), p. 68, and (6), (2), (1).

is a maximum when $\theta = \dfrac{\nu_1 - 2}{\nu_1 + \nu_2 - 4}$, and the mean value of

θ is $\dfrac{\nu_1}{\nu_1 + \nu_2}$. Except when $\nu_1 = \nu_2$, the frequency curve is skew, and reaches the J shape when ν_1 (or ν_2) $= 2$. When $\nu_1 = \nu_2 = 2$, the c.f. from 0 to θ reduces to $\displaystyle\int_0^\theta d\theta$. Thus all values of $b(1, 1)$ are equally frequent. There is no diminishing sequence of frequencies to enable us to establish unique confidence ranges. Hence, if we have six statistically independent normal variates $[x]$ from identical distributions divided into two sets of three, the fraction

$$\frac{\overset{3}{\underset{1}{S}}(x_r - \bar{x}_1)^2}{\overset{3}{\underset{1}{S}}(x_r - \bar{x}_1)^2 + \overset{3}{\underset{1}{S}}(x_s - \bar{x}_2)^2}$$

has no relatively rare values. It is like a ticket in a common lottery.

In ordinary cases, however, when both ν_1 and $\nu_2 > 2$, there is no difficulty in establishing confidence ranges and zones of rarity. For example, if $\nu_1 = 4$, $\nu_2 = 12$,

$$\frac{S_1}{S_1 + S_2} = \frac{\chi_4{}^2}{\chi_4{}^2 + \chi_{12}{}^2} = b(2, 6)$$

The modal or most frequent value is $\dfrac{2}{12} = 0 \cdot 167$. The mean value is $\dfrac{4}{16} = 0 \cdot 25$. As the variate ranges from 0 to 1, the frequency curve is clearly very skew. Using Pearson's table of $b(6, 2)$ we find that the frequency of values $< 0 \cdot 0534$ is $0 \cdot 05$, and of values $> 0 \cdot 5207$ is also $0 \cdot 05$. Zones of greater or less rarity may be taken from the Beta table.

Considering now the ratio $\dfrac{S_1}{S_2}$, if $\dfrac{S_1}{S_1 + S_2} = \alpha$, then $\dfrac{S_1}{S_2} = \dfrac{\alpha}{1 - \alpha}$ and $\dfrac{S_2}{S_1} = \dfrac{1 - \alpha}{\alpha}$. Instead of taking $\dfrac{S_1}{S_2}$, i.e. $\dfrac{\chi_4{}^2}{\chi_{12}{}^2}$, R. A. Fisher takes $\dfrac{\frac{1}{4}\chi_4{}^2}{\frac{1}{12}\chi_{12}{}^2}$ in analogy with the square of a t variate. The frequency with which $\dfrac{S_1}{S_1 + S_2}$ has values from $0 \cdot 5207$ to 1 is the frequency with which $\dfrac{\frac{1}{4}\chi_4{}^2}{\frac{1}{12}\chi_{12}{}^2}$

has values from $\dfrac{\frac{1}{2}(0\cdot5207)}{0\cdot4793}$ to ∞, i.e. $>3\cdot26$. The frequency with which $\dfrac{S_1}{S_1+S_2}$ has values from 0 to $0\cdot0534$ is the frequency with which $\dfrac{\frac{1}{2}\chi_{12}^2}{\frac{1}{4}\chi_4^2}$ has values from $\dfrac{\frac{1}{8}(0\cdot9466)}{0\cdot0534}$ to ∞, i.e. $>5\cdot91$. Thus we have $5\cdot91$ and $3\cdot26$ as the " 5 per cent. points " shown in Fisher and Yates, *Statistical Tables*, 1938, Table V.

The c.f. of Fisher's ratio $F=\dfrac{1}{\nu_1}\chi_{\nu_1}^2\Big/\dfrac{1}{\nu_2}\chi_{\nu_2}^2$ may be derived immediately from that of the corresponding Beta variate $b\left(\dfrac{\nu_1}{2},\dfrac{\nu_2}{2}\right)$ by the substitution $\theta=\dfrac{\nu_1 F}{\nu_2+\nu_1 F}$, which gives

$$\frac{\nu_1^{\frac{1}{2}\nu_1}\nu_2^{\frac{1}{2}\nu_2}\Gamma\left(\dfrac{\nu_1+\nu_2}{2}\right)}{\Gamma\left(\dfrac{\nu_1}{2}\right)\Gamma\left(\dfrac{\nu_2}{2}\right)}\int_0^{F}\frac{F^{\frac{1}{2}\nu_1-1}dF}{(\nu_2+\nu_1 F)^{\frac{1}{2}(\nu_1+\nu_2)}} \tag{13}$$

In his earlier computations of this integral, done a decade before the appearance of Pearson's Tables of the Incomplete Beta Function, Professor Fisher found it convenient to use the transformation $z=\frac{1}{2}\log_e F$ and to prepare tables of the value of z. Hence the " z test ". Tables of both z and F are included in the volume cited. Tables of F, as conversions of Fisher's z tables, were first published at Iowa, U.S.A.[14]

It is easily seen that Cauchy's variate, considered as the ratio of two statistically independent standard normal variates, may be derived similarly from $b(\frac{1}{2},\frac{1}{2})$ and expressed as $\pm\sqrt{F}$ where $\nu_1=\nu_2=1$. It may also be regarded as t_1.

A clearer view of the fundamental relationships among the basic distributions may be obtained by noting that continued integration by parts of the cumulative frequency (or " distribution function ") of $b\left(\dfrac{\nu_1}{2},\dfrac{\nu_2}{2}\right)$ produces terms of the expansion of the binomial $\{\theta+(1-\theta)\}^{\frac{1}{2}(\nu_1+\nu_2)-1}$, just as integration of the Gamma cumulative frequency produces

[13] See (1), (5) and Integration, R. P. Gillespie, 1939.

[14] Statistical Methods, G. W. Snedecor, 1938, p. 184.

successive terms of the exponential expansion ; and as the exponential (Poisson) and normal are limiting forms of the binomial, so it is easy to see that as either ν_1 or ν_2 becomes large, the Beta c.f. approaches the Gamma form, and as both become large it approaches the normal form.

IX. Consistency and Parameter Variates.

However we divide a set of n statistically independent variates which, by hypothesis, are normally distributed with common mean A and standard deviation σ, we can always obtain $(n-2)$ *consistency variates* of the Beta type (translatable into Student's t or Fisher's F or z variates), and two *parameter variates*, viz. one Beta variate (translatable into Student's t_{n-1}) involving the parameter A, and one Gamma variate $(=\frac{1}{2}\chi_n{}^2)$ involving both A and σ, all these n new variates being statistically independent. In the particular case of division into two sets we have so far noted only (n_1-2+n_2-2+1) or $(n-3)$ consistency variates. To obtain the remaining one of this sort we replace the standard normal variates

$$\frac{\sqrt{n_1}.(\bar{X}_1-A)}{\sigma}, \quad \frac{\sqrt{n_2}.(\bar{X}_2-A)}{\sigma}$$

by the two

$$\frac{\bar{X}_1+\bar{X}_2-2A}{\sigma}\bigg/\sqrt{\frac{1}{n_1}+\frac{1}{n_2}}, \quad \frac{\bar{X}_1-\bar{X}_2}{\sigma}\bigg/\sqrt{\frac{1}{n_1}+\frac{1}{n_2}},$$

which also are statistically independent of one another, of the $(n-3)$ consistency variates, and of $\dfrac{S_1+S_2}{\sigma^2}$ or $2c\left(\dfrac{n_1+n_2-2}{2}\right)$, which have been obtained in the course of successively compounding the Gamma variates $c(\frac{1}{2})$. Continuing this process one step further we obtain a Beta variate $b\left(\frac{1}{2}, \dfrac{n-2}{2}\right)$ which is translatable into the t_{n-2} variate

$$\frac{\bar{X}_1-\bar{X}_2}{\sqrt{\dfrac{1}{n_1}+\dfrac{1}{n_2}}}\bigg/\sqrt{\frac{1}{n-2}(S_1+S_2)}$$

Frequent use is made of this t_{n-2} variate to test the effect of varying one factor in an experiment, which is valid if no other of these statistically independent consistency variates shows a rare value when due account is taken of possible permutations. A rare value of any one of them

indicates unacceptability of some part of the hypothesis, (1) Gaussian distribution of each, (2) common mean, (3) common variance, or, at any rate, unreliability of the results as a means of inference. Moderately rare values of more than one might with equal cogency indicate unacceptability.

In the case of one of the t variates of the separate sets showing a rare value, we may, if sufficiently assured by previous experience that the type of experiment leads to Gaussian or "normal" distributions, reject the relevant observation, and proceed to analyse in the same way the remaining $(n-1)$ observations. Either $\overline{X}_1$ or $\overline{X}_2$ and S_1 or S_2 will thereby be modified.

In the more difficult case of Fisher's variate $\dfrac{S_1}{S_2}$ showing a rare value, we may reject the hypothesis of common variance and obtain a confidence range for the ratio $k = \dfrac{\sigma_1^2}{\sigma_2^2}$ by means of the Beta variate

$$\frac{S_1/\sigma_1^2}{S_1/\sigma_1^2 + S_2/\sigma_2^2} = \frac{S_1}{S_1 + kS_2} = b\left(\frac{\nu_1}{2}, \frac{\nu_2}{2}\right)$$

This will provide material for testing $\overline{X}_1 - \overline{X}_2$ by means of the t_{n-2} variate

$$\frac{\overline{X}_1 - \overline{X}_2}{\sqrt{\dfrac{k}{n_1} + \dfrac{1}{n_2}}} \bigg/ \sqrt{\frac{1}{n-2}\left(\frac{S_1}{k} + S_2\right)}$$

FURFURALDOXIME AS A CHELATE GROUP.

PART II. PALLADIUM COMPOUNDS WITH α (SYN) FURFURALDOXIME.[*]

By A. BRYSON, B.Sc.App., M.Sc., and F. P. DWYER, M.Sc.

α Furfuraldoxime is a white crystalline solid, m.p. 74-75°, moderately soluble in water, and extremely soluble in alcohol and acetone. Its constitution was confirmed by Brady (*J. Chem. Soc.*, (1927), 1959), who showed that treatment with acetic anhydride gave the acetyl derivative, and hence the oxime had the syn structure I.
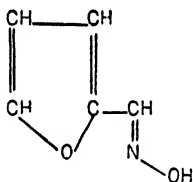
I

Assuming that the nuclear oxygen has donor properties, this compound may be considered to be analogous to β benzilmonoxime II, and might be expected to yield internal metallic complexes with Cu^{II}, Ni, Pd^{II}, and Co^{II}.
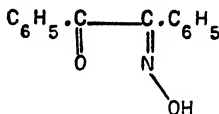
II

Curiously enough this expectation has not been realised ; palladium alone of all the common metals forms complexes with α furfuraldoxime—a circumstance which recalls the

behaviour of β benzildioxime which forms an internal complex with palladium alone (Dwyer and Mellor, THIS JOURNAL, (1935), *68*, 107).

Since the distribution of the bonds about this metal is planar (*Chem. Soc. Ann. Reports*, (1935), 161), cis/trans isomers of palladium bis α furfuraldoxime might be expected. One covalent bis complex only has been isolated—probably the trans form. This failure is due no doubt to generally recognised loose coordination in palladous complexes, except those with powerful chelate groups such as benzylmethylglyoxime (Dwyer and Mellor, *J. Am. Chem. Soc.*, (1935), *57*, 605), and diamines such as isobutylenediamine and stilbenediamine (Lidstone and Mills, *J. Chem.*, (1939), 1754).

An alcoholic solution of α furfuraldoxime added to a neutral solution of sodium chloropalladite gave an orange amorphous precipitate of the compound $Pd(C_5H_4O_2N)_2$. Since this compound was freely soluble in organic media, it is probably an internal metallic complex and the structure III has been assigned.
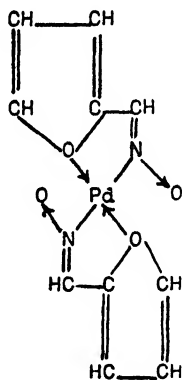
III

On standing in the solid state or in acetone solution the compound became quite insoluble in acetone, and sparingly soluble in most organic solvents except chloroform. The new compound had the same empirical formula $Pd(C_5H_4O_2N)_2$ but was proved to be trimeric. In boiling chloroform with pyridine or p-toluidine the compound gave no evidence of further coordination and must be formulated as in IV with the terminal oxime groups acting as chelate groups.

H_4C_5 — O — Pd — $NO.C_5H_4O$ — Pd — $NO.C_5H_4O$ — Pd — O — C_5H_4
ON — $OC_5H_4.ON$ — $OC_5H_4.ON$ — NO
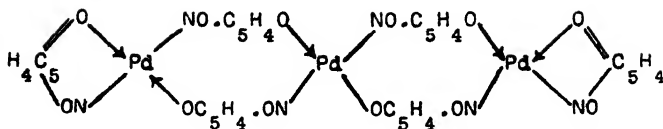
IV

With cold pyridine III gave the water soluble compound V, whose constitution as the bispyridine palladous oximate was confirmed by its transformation into the well known bispyridine palladous chloride, $Pd(C_5H_5N)_2Cl_2$, by treatment with cold dilute hydrochloric acid. The substance V was also freely soluble in chloroform, indicating a dynamic equilibrium between the truly ionic oximate form and a wholly covalent form (VI).

$$(Pd (C_5H_5N)_2)^{++} . (C_5H_4O_2N)_2$$

V

$C_5H_4O_2N$ — Pd — NC_5H_5
$C_5H_4O_2N$ — NC_5H_5
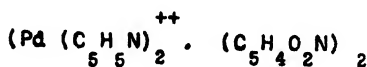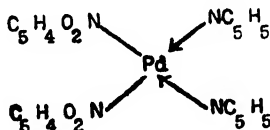
VI

The trimeric substance (IV) when heated in pyridine solution to 85-90° was degraded ultimately to the bispyridine compound (V) or (VI). The first step was the breaking of the coordinate linkages of the terminal oxime groups, followed by the addition of two molecules of pyridine to yield the compound (VII). This compound then broke down at the coordinate bridges to yield three molecules of the bispyridine compound (V) or (VI).

$C_5H_4O_2N$ — Pd — $NO.C_5H_4O$ — Pd — $NO.C_5H_4O$ — Pd — $NO_2C_5H_4$
C_5H_5N — OC_5H_4ON — $OC_5H_4.ON$ — NC_5H_5
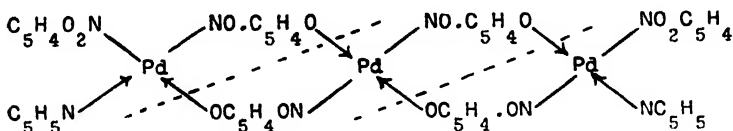
VII

Both (III) and (IV) gave the same monoethylene-diamine compound $Pd(C_5H_4O_2N)_2 . C_2H_8N_2$, which was freely soluble in water and in organic media such as chloroform, and hence constituted like the bispyridine compound (V), (VI). The monoethylenediamine compound by treatment with further ethylenediamine gave the

ionic water-soluble bis compound which was quite insoluble in organic media.

EXPERIMENTAL.

Palladium bis α furfuraldoxime. Monomeric Form.

A cold aqueous alcoholic solution of α furfuraldoxime (1·5 gm.) was added to a cold neutral solution of sodium chloropalladite (0·75 gm. Pd), and sodium acetate added. The resultant voluminous orange yellow precipitate after several washings with water was dissolved in cold acetone in which it was completely soluble, and precipitated with water. Provided that these operations were performed rapidly very little transformation to the trimeric form occurred. The compound which could not be obtained in crystalline form decomposed without melting, and was freely soluble in organic media to orange red solutions. Since the transformation to the trimeric form is probably a reaction of the third order, and hence almost independent of the temperature, the molecular weight was determined in acetone by the boiling point method. At the end of the determination the acetone insoluble trimeric form was filtered off, weighed, and a correction applied.

Found : Pd =32·60% ; mol. wt.=386,398 ; calculated for $Pd(C_5H_4O_2N)_2$: Pd =32·45% ; mol. wt. =328·7.

Palladium bis α furfuraldoxime. Trimeric Form.

A concentrated acetone solution of the monomeric form was allowed to stand for 48 hours at room temperature. At the end of one hour a crystalline precipitate had commenced to come down, and at the end of 48 hours approximately 75% of the monomer had been transformed. The same transformation occurred in the solid state by keeping at room temperature. The substance after crystallisation from chloroform and petroleum ether gave small orange yellow monoclinic tablets and prisms, insoluble in acetone, slightly soluble in alcohol and benzene, but easily soluble in chloroform. On heating the compound decomposed without melting.

Found : Pd =32·34% ; mol. wt. =1057, 972 (in chloroform, ebullioscopic) ; calculated for $(Pd(C_5H_4O_2N)_2)_3$: Pd =32·45% ; mol. wt. =986.

Recovery of the Oxime.

Since α furfuraldoxime is easily transformed to the β isomer in the presence of acids and metallic salts (Bryson

and Dwyer, This Journal, (1940), *74*, 107), both substances were tested to determine whether the α oxime was still present. Each form of the palladium compound (0·2 gm.) was treated with two drops of caustic soda solution (2N) and 5 c.c. of 2N potassium cyanide solution. On shaking the whole of the substance passed into solution, and the mixture was then poured into cold ammonium chloride solution and extracted with ether. Evaporation of the solvent gave a crude substance which melted in each case at 70° C., and after crystallisation at 73-74°. Hence the oxime had not undergone any change.

Bispyridine Derivative (V), (VI).

The freshly precipitated monomeric form of palladium bisfurfuraldoxime without crystallisation or drying was dissolved in cold pyridine, in which it gave an orange yellow solution. Solid potassium carbonate was then added to dry the solution, which was subsequently precipitated with petroleum ether. The pale lemon yellow microcrystalline powder was extremely soluble in water and alcohol, and fairly soluble in chloroform. Pyridine was lost at 100-110°.

Found: $Pd = 21·70$; calculated for $Pd(C_5H_4O_2N)_2.2C_5H_5N$: $Pd = 21·93\%$.

Dissolved in cold water and treated with a few drops of cold 2N hydrochloric acid, the compound gave a creamy white precipitate of minute needles of bispyridine palladous chloride.

Found : $Pd = 31·62\%$; calculated for $Pd(C_5H_5N)_2Cl_2$: $Pd = 31·78\%$.

Reaction of the Trimeric Form with Pyridine and p-Toluidine.

The trimeric form (1 mol.) was treated in chloroform solution with exactly 2 mols. of p-toluidine and allowed to stand at room temperature for 15 mins. The solvent was then removed under reduced pressure, and the residue examined with the microscope, when it was found to consist of unchanged trimer and p-toluidine. In a second experiment the trimer (1 mol.) was refluxed in chloroform solution with pyridine (6 mols.) for one hour. At the end of this time the mixture was precipitated with petroleum ether. The resulting precipitate was found to contain no pyridine—hence it was concluded that the trimeric form was coordinately saturated. The degradation of the compound was achieved by heating a suspension in

pyridine to 80-90°, when the whole passed into an orange yellow solution. Immediate cooling followed by precipitation with petroleum ether gave a yellow precipitate. This was extracted with cold water, and evaporation of the solvent under vacuum gave pale yellow crystals of the compound bispyridine-bisfurfuraldoxime palladium (see above). The residue from the water extraction still contained pyridine, and was identified as a coordination compound of the trimer containing two molecules of pyridine. This yellow microcrystalline compound was sparingly soluble in alcohol, but easily soluble in chloroform. Pyridine was easily lost on heating.

In a typical experiment 1·44 g. of the trimeric form of bisfurfuraldoxime palladium by heating to 85° with pyridine gave 0·834 gm. of the compound $(Pd(C_5H_4O_2N)_2)_3 . 2C_5H_5N$, and 0·723 gm. of $Pd(C_5H_4O_2N)_2 . 2C_5H_5N$. When the bispyridine derivative of the trimer was dissolved in pyridine and heated to 90°, it broke down gradually to the water-soluble $Pd(C_5H_4O_2N)_2 . 2C_5H_5N$.

Found : Pd $=28·13\%$, $C_5H_5N =13·97$; calculated for $(Pd(C_5H_4O_2N)_2)_3 . 2C_5H_5N$: Pd $=27·98\%$, $C_5H_5N = 13·89\%$.

Monoethylenediamine Derivative.

The trimeric form (1 mol.) in cold chloroform was treated with exactly three mols. of anhydrous ethylenediamine in benzene solution. The colour lightened slightly and after a few minutes a faint white precipitate commenced to come down. The formation of this precipitate could be hastened by heating. The precipitate, which was of small amount (and subsequently identified as the bisethylenediamine derivative), was filtered off, and the yellow solution precipitated with petroleum ether. The resulting yellow amorphous powder was extremely soluble in water, and quite hygroscopic. It was also soluble in chloroform—and hence may be considered as ethylenediamine palladous oximate in dynamic equilibrium with ethylenediamine bis furfuraldoxime palladium.

The same compound was obtained from the monomeric form of bisfurfuraldoxime (1 mol.) and ethylenediamine (1 mol.).

Found: Pd $=27·50\%$; calculated for $Pd(C_5H_4O_2N)_2.C_2H_8N_2$: Pd $=27·45\%$.

Bisethylenediamine Derivative.

The monoethylenediamine derivative treated with an additional molecule of ethylene diamine in warm chloroform solution gave a fine very pale yellow precipitate of the required compound. The compound can be obtained direct from either the monomeric or trimeric form of bisfurfuraldoxime by treatment with ethylenediamine in chloroform solution. The compound was easily soluble in water or methyl alcohol (crystallises in needles by slow evaporation of this solvent), but quite insoluble in chloroform or benzene—and hence must be considered as the ionic bisethylenediamine palladous oximate.

Found :　　　$Pd = 23 \cdot 73\%$;　　　calculated　　　for $Pd(C_5H_4O_2N)_2 \cdot 2C_2H_8N_2$:　$Pd = 23 \cdot 78\%$.

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THE LOWER MIDDLE DEVONIAN RUGOSE CORALS OF THE MURRUMBIDGEE AND GOODRADIGBEE RIVERS, N.S.W.

By DOROTHY HILL, M.Sc., Ph.D.

(With Plates IX-XI.)

Seventeen species are described, of which eight are new. The age indicated by the whole fauna is Couvinian. The Rugose faunas of the successive limestones near Cavan are listed ; that of the lowest (Bluff) limestone indicates either the beds transitional from the Coblenzian or the very base of the Couvinian ; the rather higher Sponge limestone may represent part of the Upper Couvinian.

The Devonian of the Murrumbidgee and Goodradigbee Rivers is regarded by Harper (1909) as a syncline, with lavas at the base, limestones and shales following, and tuffs above. On the eastern side of the syncline, at Cavan, he subdivided the limestones as follows : —From the base upwards : chocolate coloured volcanic ash, with shales and limestone bands, 150 ft. ; the Bluff limestone, 150 ft. ; the Yellow limestone, 400 ft. ; the Currajong limestone, 200 ft. ; upper beds of basal limestone series, 1,500 ft. ; siliceous shales and quartzites, with several lenticular beds of limestone, 1,800 ft. ; second limestone series, thickness unknown. The corals described below from Cavan, Taemas, and Goodhope are from the basal limestones. On the western side of the syncline, along the Goodradigbee R., the limestone series is still undivided, and the corals from Wee Jasper and Cave Flat are from unknown horizons therein. The Sponge limestone (Dun MS.), which is within the upper beds of the basal limestone series, is probably the equivalent of the *Receptaculites* limestone (Shearsby MS.) of Por. 208, Par. Waroo.

The following list gives the species described and their occurrences :

Some of the Tabulata, which are not, however, described herein, were collected from the limestones as follows :

Favosites bryani Jones	..	.. *Receptaculites* Lst.
F. murrumbidgeensis Jones	..	.. .. Bluff Lst.
Gephuropora duni Etheridge	..	Bluff, Currajong Lsts.
Coenites expansus de Koninck		Sponge Lst., *Receptaculites* Lst., Wee Jasper

Age. Of the fauna of the Bluff limestone, *Acanthophyllum æquiseptatum* and " *C.*" aff. *australe* are similar to species from the Chaudefonds limestone of France, transitional between Lower and Middle Devonian ; *Disphyllum gemmiforme, Thamnophyllum abrogatum* and *T. curtum* have no close relatives, but the latter genus is known only from the Lower and Middle Devonian ; *Eridophyllum bartrumi* occurs also in the Middle Devonian of Reefton, New Zealand, and *Mictophyllum trochoides* is similar to *M. cresswelli* from the Lower or Middle Devonian of Lilydale, Victoria. On the whole this evidence suggests a horizon somewhere near the base of the Couvinian, or perhaps the top of the Coblenzian. The two species of the Currajong limestone, " *Campophyllum* " *recessum* and *Gephuropora duni*, are known also from the Middle Devonian of Buchan, Victoria. *Xystriphyllum mitchelli* suggests for the Sponge limestone an upper Couvinian horizon, as a very similar form occurs in a limestone thought to be Upper Couvinian at Clermont, in Queensland, but *Favistella* sp., which occurs with it, resembles European forms from the Upper Ludlow and Lower Devonian. " *Cystiphyllum* " cf. *americanum* from the *Receptaculites* beds, probably the equivalent of the Sponge limestone, is comparable with American and European Givetian species.

The fauna from the undifferentiated limestones along the Goodradigbee R. suggests the Couvinian. Thus *A. asper* is very like a French species from beds thought to represent the transition from Lower to Middle Devonian. *A. ? clermontense* occurs in the Upper Couvinian of Clermont, Queensland, and *A.* sp. is like other specimens in the ? Lower Devonian Garra beds of the Molong district and the ? Lower Couvinian of Silverwood, Queensland. *T. curtum* and *E. bartrumi* are known in the Bluff limestone, and " *Campophyllum* " *recessum* in the Currajong. *Vepresiphyllum falciforme* is unknown elsewhere. *Pseudamplexus* aff. *princeps* seems related to ? Lower Devonian specimens

from the Garra beds. *Grypophyllum aggregatum* resembles Couvinian and Givetian European species, and *Xystriphyllum mitchelli* occurs in the Sponge limestone on the east.

Family ACANTHOPHYLLIDÆ.

Acanthophyllidæ Hill, 1939*a*, p. 56 ; 1939*b*, p. 220 ; Hill and Jones, 1940, p. 178.

Rugosa with a wide dissepimentarium of highly arched dissepiments, long septa frequently modified in the dissepimentarium, and with numerous, shallowly concave tabulæ deepened at the axis. The major septa are long and unequal, carinate in the tabularium, never amplexoid, and the two minor septa neighbouring the counter septum are longer than the rest.

Range. Gotlandian of Europe, Lower and Middle Devonian of Europe and Australia, and Upper Devonian of Europe.

Genus Acanthophyllum Dybowski.

Acanthophyllum Dybowski, 1873, p. 339 ; 1874, p. 493 ; Hill, 1939*a*, p. 56 ; 1939*b*, p. 222.

Genolectotype : Cyathophyllum heterophyllum Edwards and Haime, 1851, pl. x, figs. 1*a-c*. Devonian, Eifel, Germany.

Diagnosis. Solitary or sub-compound Rugosa with a wide dissepimentarium of small, highly arched dissepiments, with shallowly concave, axially deepened tabulæ, and with long but unequal major septa. The axial ends of the major septa are arranged in groups in the tabularium, and are straight or curved vortically, the curvature differing in degree from group to group ; the cardinal septum is typically short, and one septum, not a protoseptum, extends to the axis. The septa show different types of modification ; they are frequently much dilated, either in the dissepimentarium, or more rarely in the tabularium, or in both ; towards the periphery they may be thin and lined with lateral dissepiments ; in the tabularium they are typically waved and carinate.

Range. ? Ludlovian of Gotland, Lower and Middle Devonian of Europe and Australia, and Upper Devonian of Europe.

Acanthophyllum æquiseptatum sp. nov.

(Plate IX, figs. 1, 2.)

Holotype. F 9577, Australian Museum, Clear Hill, near Taemas Bridge, Murrumbidgee River, N.S.W. Collected by A. J. Shearsby, 1904. Lower Middle Devonian. Plate IX, figs. 1a, b.

Diagnosis. Acanthophyllum with minor and major septa slightly and equally thickened, and directed radially even in the tabularium, which is narrow.

Description. The corallum is apparently solitary, trochoid or trocho-cylindrical, attaining a diameter of 22 mm., when there are 29 major and 29 minor septa, all slightly and equally thickened ; the thickening is greatest at their bases, which are in contact inside the epitheca, and is least just inside this stereozone. The septa keep remarkably well to a radial course, even in the tabularium, though there is minor waviness here and there. The major septa are unequal, and extend almost to the axis, there often being small pieces near the axis of a transverse section appearing discontinuous with the main part of the septum. Those parts in the tabularium are carinate. The longest septum is not a proto-septum. The minor septa extend three-quarters of the way to the axis, i.e., to the inner edge of the dissepimentarium, except for the two neighbouring the counter septum, which are longer. The tabularium is narrow, occupying only one-quarter the diameter of the corallite. The tabular floors are depressed with an axial deepening, and the tabulæ are incomplete, close, and with but very shallow arching. The dissepiments are small, rather globose, and arranged in floors which are but slightly inclined near the periphery, but steepen towards the tabularium. In transverse section many are geniculate, with their angles pointing outwards. A few lateral dissepiments are attached to the sides of the septa.

Remarks. My specimens are from the Bluff limestone, on Clear Hill and on the Wee Jasper road half a mile from Taemas Bridge. They are close to *Cyathophyllum torquatum* Schlüter, Le Maitre (1934, pl. v, figs. 16, 17) from the Chaudefonds limestone, at the transition between Lower and Middle Devonian.

Acanthophyllum asper sp. nov.

(Plate IX, figs. 3, 4.)

Holotype. F 4270, University of Queensland Collection (Hill, 1938), first karst on Cave Flat road from Wee Jasper, N.S.W. Lower Middle Devonian.

Diagnosis. Trochoid *Acanthophyllum* with thick septa, their greatest dilatation being in the tabularium.

Description. The corallum is solitary and trochoid, the holotype expanding from 10 mm. to 28 mm. in a height of 25 mm. The calice is not seen, but from the dissepimental floors appears to have had a steeply sloping platform. There are 28 major septa alternating with 28 minor septa at a diameter of 20 mm. The major septa are unequal and long, extending to the axis, the longest apparently being the cardinal septum ; they are straight in the dissepimentarium, and a little curved and carinate in the tabularium ; they are thick throughout, with roughened or carinate sides, but are thicker in the tabularium than elsewhere except at the periphery, where they are dilated wedge-wise in contact, forming a narrow stereozone. The minor septa are only half as long as the major, so that the tabularium occupies half the diameter of the corallite. Those neighbouring the counter septum are longer than the others. The tabular floors are concave with a median depression, and the tabellæ are thin, only very slightly arched, and crowded. The dissepiments are globose and of moderate size, being arranged in floors sloping rather steeply into the tabularium ; some floors are reinforced by thickening.

Remarks. Thickening of ·the septa in the tabularium was shown by Wedekind to be characteristic of Acanthophyllids in the base of the Middle Devonian of the Eifel. Our species also resembles very closely *Cyathophyllum dianthus* Goldfuss, Le Maitre (1934, pl. v, figs. 13, 14) from the beds transitional between Lower and Middle Devonian at Chaudefonds, France.

Acanthophyllum ? clermontense (Etheridge).

(Plate IX, fig. 5.)

Acanthophyllum ? *clermontense* (Etheridge) ; Hill, 1939a, p. 58, pl. iv, figs. 3a-b, Couvinian, Douglas Ck., Clermont, Queensland.

Diagnosis. Large *Acanthophyllum* with a very narrow tabularium, large dissepiments and smooth septa.

Remarks. One specimen, F 5658 (Australian Museum, slide No. 716 from Cave Flat, Murrumbidgee R., Lower Middle Devonian), very closely resembles the specimen from Clermont referred to above. It has 30 unequal major septa interdigitating in the tabularium, at a diameter of 48 mm., the alternating minor septa being very long, extending seven-eighths of the way to the axis, leaving only a very narrow tabularium. The septa are slightly and equally thickened and lateral dissepiments are very rare. The dissepiments are rather large and distant. The Cave Flat specimen differs from the Clermont specimen only in having minor septa equally as thick as the major ; in the latter the minor septa are appreciably thinner. The Clermont specimen, being the only one with its particular morphology, was regarded as doubtfully belonging to *Acanthophyllum clermontense*, with which it occurs, but which differs in having closer and more carinate septa, with more lateral dissepiments, and in general smaller dissepiments. But there was insufficient material for a full knowledge of the variability of the species. The discovery of only one specimen in the Cave Flat limestone, while it suggests that the morphology represents a species separate from *A. clermontense*, certainly does not prove it, as we know nothing of the variability of the species at Cave Flat, and for the present the two specimens are doubtfully referred to *A. clermontense*.

Acanthophyllum sp.

(Plate IX, fig. 6.)

One specimen, F 4273, University of Queensland Collection, from the first karst on the Cave Flat road from Wee Jasper, is slenderly cylindrical, about 12 mm. in diameter, with a narrow dissepimentarium, and slightly and equally dilated septa, bearing small lateral spines. It appears similar to a specimen figured from the ? Lower Devonian Garra Beds (Hill and Jones, 1940, pl. II, fig. 1), and to another described from the Couvinian of Silverwood, Queensland (Hill, 1940*a*, pl. II, fig. 2).

Family CANINIIDÆ.

Caniniidæ ; Hill, 1939*c*, p. 102.

Simple Rugose corals with an open tabular fossula ; the septa are typically dilated and amplexoid in the wide tabularium, and frequently discontinuous in the dis-

sepimentarium ; the tabulæ are complete, domed or flat, and downturned at the edges.

Age. Carboniferous and Permian. Possible representatives are known from the Upper Devonian, and if the species described below belongs to the family, as seems possible, from the Middle Devonian also.

Genus "Campophyllum" auctt.

Edwards and Haime, 1850, p. lxviii, founded the genus with " Typ. sp. *Campophyllum flexuosum* ; *Cyathophyllum flexuosum* Goldfuss, Petref. Germ., vol. i, tab. xvii, fig. 3." From this it would seem that the lectotype of the genotype must be chosen from Goldfuss' specimens. But Frech [1885, p. 38 ; 1886, p. 183 (69)] considered that Goldfuss' specimens were from the transition zone between Devonian and Carboniferous at Aachen, and gave figures which show that they were congeneric with the genotype of *Palæosmilia* Edwards and Haime, 1848, so that *Campophyllum* would become a synonym. *C. flexuosum* Edwards and Haime *non* Goldfuss *non* Linnæus he re-named *Cyathophyllum lindstromi*. I have examined the figured specimen, which is very close to *Caninia subibicina* M'Coy from the Carboniferous, and while the latter is retained in *Caninia*, it is consistent to place the Upper Middle Devonian *C. lindstromi* therein. Prof. O. H. Schindewolf is at present studying the type of *Cyathophyllum flexuosum* Goldfuss, and no definite conclusion on the value of the name *Campophyllum* can be reached in the meantime. It has been applied by authors to septate forms with a narrow dissepimentarium and large tabulæ, and it is in this broad conception that the name is applied as " *Campophyllum* " to the Australian species described below, which is placed only very doubtfully in the Caniniidæ.

"Campophyllum" recessum sp. nov.

(Plate IX, fig. 7.)

Campophyllum gregorii Etheridge, Chapman, 1912, p. 219, pl. xxxiv, figs. 3, 4, 5, from the Middle Devonian of Bindi, and Buchan, E. Gippsland, Victoria. *Non Campophyllum gregorii* Etheridge, 1892b, p. 60, pl. iii, figs. 15-18 from the Upper Middle Devonian of Reid Gap, Queensland.

Holotype. F 16343, Australian Museum (Dun collection), Lower Middle Devonian, Devil's Elbow, Murrumbidgee R., opposite island, Bloomfield's station.

Diagnosis. Rugosa probably solitary but living in communities ; trochoid or ceratoid, with average diameter about 10 mm. ; the septa are short, thin and recessive from the axis, the recession leaving inosculating dissepiments ; the tabularium is wide and the tabulæ are horizontal and complete, or depressed and incomplete.

Description. The corallum is apparently solitary, as the individuals are trochoid or ceratoid, of rather irregular growth, but they occur together in large numbers, usually to the exclusion of other forms, evidently living in communities. The average adult diameter is about 10 mm., when there are 22 major and 22 minor septa, but 16 mm. may be attained. The major septa usually do not extend more than one-third of the way to the axis, but in some sections thin discontinuous extensions may be seen running towards the axis. The major septa are unequal in length, and this seems to be due to their unequal withdrawal. They thicken a little towards the periphery, where the layer of thickening turns at right angles to the septa to form a narrow lining to the epitheca. The minor septa are shorter than the major, and seldom extend to the inner margin of the dissepimentarium ; they have a similar peripheral thickening to the major septa. The tabularium is wide ; the tabulæ are usually complete and horizontal, close or distant, occasionally reinforced by small plates at the margins ; they may be sagging, however, and are sometimes incomplete. The dissepiments are in one to four series, the outermost being the largest and the most regular ; they are small and steeply inclined, sometimes elongate ; in transverse sections they may have angular intersections when the septa are much withdrawn.

Remarks. I know of no closely comparable species in Europe or America except the specimen from the Middle Devonian Hillesheim beds figured by Wedekind (1925, figs. 97-99) as *Campophyllum* sp. Our species differs, however, in the irregular recession of the septa from the axis, and in not having the septal ends within the tabularium dilated. Our southern species differs from *C. gregorii* Etheridge from the Upper Middle Devonian of the Reid R. in Queensland, for the latter has dilated, non-recessive, equal septa, and globose dissepiments suggesting relation to the Disphyllidæ.

Localities. In addition to the locality, in the Cavan area the species occurs in the Currajong limestone on the road to Wee Jasper 0·6 mile from the new Taemas bridge.

It also occurs at Spring Ck., Buchan, Victoria, and at Bindi, E. Gippsland, in Lower Middle Devonian beds.

CYSTIMORPHS.

Cystimorphs ; Hill, 1939b, p. 248.

"Cystiphyllum" aff. australe Etheridge

(Plate IX, figs. 10, 11.)

Cystiphyllum (? *Microplasma*) *australasica* ; Etheridge, 1902, p. 256, pl. xxxix, figs. 3, 4 ; pl. xl, figs. 3, 4 ; *pars*, i.e. those specimens from the Murrumbidgee. Not necessarily *Cystiphyllum americanum* Edwards and Haime var. *australe* Etheridge, 1892b, p. 58, pl. iii, figs. 13, 14 (called *australica* in explanation to plate), from the Givetian of the Reid Gap, North Queensland.

? " *Cystiphyllum* " sp., Hill, 1939b, p. 250, pl. xv, figs. 4, 5, Lower Devonian, Loyola, Victoria.

Description. The corallites are usually found aggregated parallel, suggesting that they form phaceloid colonies ; no evidence of increase has been found, however. The individuals appear to be gradually increasing in diameter, up to 27 mm. Horizontal skeletal elements are dominant ; they are distally arched and are roughly divisible into a peripheral zone of steeply inclined, smaller plates, and an axial zone about half the diameter of the corallite, of larger, more swollen and more loosely packed plates, arched about planes which are nearly horizontal. In the peripheral zone the plates are more swollen at the distal end than at the proximal, and such swollen plates give a truncated oval section when the corallites are cut transversely. The plates are somewhat dilated, the dilatation tending to have maxima along calical floors which succeed one another at about 3 or 4 mm., the plates belonging to intermediate floors being less swollen. The dilatation may increase a little from axis to periphery, but it is not noticeably greater in any one zone. The dilating tissue may be seen to contain septal trabeculæ, and in places these are produced into tooth-like projections, seemingly commoner near the periphery than near the axis. The trabeculæ are monacanths and not holacanths. There is a narrow stereozone about 1 mm. wide inside the epitheca.

Remarks. The Clear Hill (Bluff limestone) specimens resemble that figured by Le Maitre (1934, pl. vi, figs. 15, 16) from the Chaudefonds limestone at the transition between Lower and Middle Devonian in France. This has the same type of thickening, and the same tendency for monacanths to project from the thickened dissepiments in

peripheral zones. They also appear close to the specimen from Loyola, Victoria, mentioned in the synonymy, but in that form the dilatation appeared to increase towards the periphery. They are also quite close to the lower Givetian forms figured by Wedekind and Vollbrecht (1931) and by Sochkina (1936) as *Lytophyllum*, which appears to belong to the same general group as *Cystiphyllum pseudoseptatum* Schulz from the Middle Devonian of the Eifel, and *Cystiphyllum americanum* Edwards and Haime (see Fenton and Fenton, 1938) from the Middle Devonian of U.S.A.

The Givetian Reid Gap specimens called *australe* by Etheridge differ in having thickening less generally developed, dilatation being practically confined to the narrow peripheral stereozone. The Reid Gap and Taemas specimens, however, are thought to form a related group.

The internal structure of *Mesophyllum lonense* Stumm (1937, p. 440, pl. 55, fig. 11) from the Couvinian of the Nevada limestone is very similar.

"Cystiphyllum" americanum Edwards and Haime.

Cystiphyllym americanum Edwards and Haime, 1851, p. 464, pl. xiii, figs. 4-4a ; Fenton and Fenton, 1938, p. 228, which see for references and figures, and full description.

"Cystiphyllum" cf. americanum Edwards and Haime.
(Plate X, fig. 1a and 1b.)

Material. Several specimens and fragments from the Lower Middle Devonian *Receptaculites* beds in Por. 208, Par. Waroo, Murrumbidgee R., N.S.W., now F 4297-4304, F 4306-4307, University of Queensland collection.

Remarks. These specimens differ from " *C.*". aff. *australe* described above and resemble that part of "*C.*" *americanum* called *C. varians* by Hall (see figure in Fenton and Fenton, 1938, p. 227), in being large and turbinate with a talon, i.e. an arched lateral expansion acting as an anchor and a prop to the corallum. Also, the only sections available show undilated horizontal skeletal elements, without any traces of septa or trabeculæ based on them. Fenton and Fenton have shown that such an absence of dilatation is not of specific value in the " *C.*" *americanum* group, and also that there is a very considerable variation in shape of the corallum in this group. It seems that for reliable specific determinations in these Devonian cystimorphs a much larger amount of material than is at present

available to me is necessary. The Australian forms
described above as "*C.*" aff. *australe* and "*C.*" cf.
americanum have the same general morphology as the
group known in the Hamilton (Givetian) of America as
the "*C.*" *americanum* group, and in the Givetian of Germany
as *Lithophyllum* Wedekind (1925, p. 29, Wedekind and
Vollbrecht, 1931) except perhaps for the genotype, a
group formerly known as *C. pseudoseptatum* Schulz.

Family DISPHYLLIDÆ.

Disphyllidæ Hill, 1939b, p. 224.

Rugose corals with septa which tend to be dilated and
to develop trabecular carinæ, and to have an area of
divergence of the septal trabeculæ ; with flat or gently
curved axial tabulæ, usually complete, often supplemented
by inclined, periaxial tabulæ ; and with globose dis-
sepiments which may be arranged in a vertical series of
horse-shoes to form the wall of the tabularium.

Range.   Upper Silurian of New South Wales, Devonian
of Europe, America, Australia and Asia.

Genus Disphyllum de Fromentel

Disphyllum de Fromentel, 1861, p. 302 ; for references, etc., see Lang
and Smith, 1935, p. 544 ; Hill, 1940b, p. 398.

Genotype (chosen Lang and Smith, 1934, p. 80).   *Cyatho-
phyllum cæspitosum* Goldfuss, 1826, pl. xix, fig. 2b, Middle
Devonian, Eifel, renamed *Cyathophyllum goldfussi* Geinitz,
1846, p. 569 ; see Lang and Smith, 1935, p. 568.

Diagnosis.   Phaceloid Rugose corals in which increase
may be lateral or peripheral ; the septa rarely reach the
axis, but are usually long, and typically thin ; the tabulæ
are sometimes complete, though generally incomplete and
differentiated into a transverse axial, and an inclined peri-
axial series ; with dissepiments typically small, strongly
arched, sometimes of one, but frequently of two, kinds :
an inner, single series of globose distally directed dis-
sepiments, and an outer series of flat or arched
dissepiments.

Remarks.   In Europe and North America the genus is
characteristic of the Middle and Upper Devonian.   In
Australia it occurs in the Upper Silurian and Middle
Devonian.

Disphyllum gemmiforme (Etheridge).
(Plate X, figs. 2, 3.)

Disphyllum gemmiformis Etheridge, 1902, p. 253, pl. xxxvii, fig. 1,
   pl. xxxix, figs. 1, 2, pl. xl, fig. 1 ; Middle Devonian Cave Lime-
   stone, Taemas district, N.S.W.

Holotype. F 5171, Australian Museum collection, from
Taemas Bridge Road, north bank of Murrumbidgee R.,
figured Etheridge, *id.* pl. xxxvii, fig. 1.

Diagnosis. Disphyllum in which increase is usually
peripheral and parricidal, the major septa are no longer
than the minor, there are no carinæ, and the tabulæ are
complete and horizontal, sometimes supplemented at the
margins by small, inclined plates.

Description. The corallum is fasciculate and spreading,
increase of the hystero-corallites usually taking place very
rapidly ; usually increase is peripheral and parricidal, but
one case appeared to be axial, three corallites occupying
the whole area of the parent. The individual corallites
are unequal, up to 10 mm. or more in diameter, but the
average is about 7 mm. When hystero-corallites first
appear they have only a narrow fringe of short equal septa.
In the adult corallite there are about 34 septa extending a
little over half-way to the axis, it being difficult to dis-
tinguish the major from the minor in many cases. The
septa are rather thin, and may be wavy or a little carinate,
the carinæ being of the xyloid type ; in younger corallites
the septa are all shorter, extending less than half-way to
the axis. The tabulæ are mostly complete and horizontal
and rather distant, but there are some irregularities, and
they may be supplemented at the margins by small
inclined plates. The dissepiments are in one to four series,
the outermost being large and rhomboid, the inner small
and globose.

Remarks. The tabularium of this species closely
resembles that of the American Couvinian *Cylindrophyllum
elongatum* and the European Givetian *D. geinitzi* ; its
weakly carinate equal septa, however, distinguish it from
these as from all other *Disphyllum*.

The specimen figured as *Acervularia luxurians* var.
breviseptata Weissermel by Sochkina (1937, pl. xvii) from
the Ludlovian of the Urals appears to have a similar
internal structure to our species, however.

Localities. The species is common at Clear Hill and
other outcrops of the Bluff limestone in the Taemas
district. It also occurs at Goodhope.

Genus Thamnophyllum Penecke.

Thamnophyllum Penecke, 1894, p. 593 ; Lang and Smith, 1935, p. 564 ; Hill, 1939b, p. 227.

Genolectotype (chosen Lang and Smith, *loc. cit.*).   *Thamnophyllum stachei* Hornes in Penecke, 1894, p. 594, pl. viii, figs. 1-3, pl. xi, figs. 1-2, from the *Barrandei* beds (upper part of Lower Devonian) and Couvinian of Graz, Austria.

Diagnosis. Dendroid Rugosa with typically straight corallites, and increase which is usually parricidal and produces four large marginal offsets which, in their earliest stages, are united by dissepimental tissue occupying the fork formed by the diverging branches.   The septa are so dilated in the dissepimentarium that the only loculi are those enclosed by a median series of horse-shoe dissepiments the trabecular dilatation of the septa being continuous over the surfaces of these dissepiments.   In the tabularium the septa are transverse, flat or slightly domed or saucered, mostly complete, and usually very widely spaced.

Range. Lower Devonian of Australia, upper part of the Lower Devonian of Austria, Lower Middle Devonian of Austria and France, and possibly Givetian of France.

Thamnophyllum abrogatum sp. nov.

(Plate X, fig. 4.)

Holotype. F 4240, University of Queensland collection (Jones and Denmead), Clear Hill, Murrumbidgee R., N.S.W.   Lower Middle Devonian.

Diagnosis.   *Thamnophyllum* with dissepiments which are globose but not horse-shoe-shaped, some being lonsdaleoid.

Description.   The corallum is dendroid and the individual corallites are straight, and from 4 to 6 mm. in diameter, and and type of increase is not known.   There are 18 major septa at a diameter of 6 mm., extending about half-way to the axis, being a little longer than the alternating minor septa, which extend about one-third of the way to the axis. Both orders are dilated, and in lateral contact, which is occasionally imperfect so that dissepiments are developed between them.   The trabeculæ of the septa show no area of divergence, all being directed upwards from the periphery of the corallite.   No epitheca is visible in transverse section.   The tabulæ are usually complete, distant, and rather corrugated, more usually a little arched rather than a little depressed.   The dissepiments are globose and

rather large, apparently seldom in more than one series, and occasional plates are larger and lonsdaleoid causing breaks in the septa. The septal thickening spreads over them.

Remarks. The holotype is the only specimen at present included in this species. It resembles *T. curtum* described below in having straight ⸱ orallites with a wide tabularium in which distant, ragged tabulæ are developed. In *T. curtum* the septa, however, appear to be equal and unthickened, and increase is by four hysterocorallites produced by axial increase, each apparently circumscribed by an epitheca. *T. curtum's* dissepimentarial characters are those of *Disphyllum gemmiforme*, and its tabularial characters those of *Thamnophyllum abrogatum*, while its increase is axial.

The holotype is doubtfully referred to *Thamnophyllum*, since its type of increase is not known, its dissepiments are not of the characteristic horse-shoe type but are frequently lonsdaleoid, and there is no area of divergence in the trabeculæ. In these two latter characters it differs from European *Thamnophyllum*, and deductions concerning its age are confined to the known limits of the genus, i.e. Lower and Middle Devonian.

Thamnophyllum curtum sp. nov.
(Plate X, fig. 5.)

Holotype. F 9905, Australian Museum (collector, Shearsby, No. 306), Boambolo or Cavan, Lower Middle Devonian, Murrumbidgee R.

Diagnosis. Phaceloid Rugosa with slender straight corallites with axial increase ; with major and minor septa short and equal, sometimes dilated and in contact ; with one or sometimes two series of globose dissepiments ; and with distant tabulæ complete and horizontal, or depressed and incomplete.

Description. The corallum is phaceloid, the individual corallites being from 4 to 6 mm. in diameter, straight, and with axial increase, three or four corallites arising simultaneously, being cerioid at the point of origin. The major and minor septa are difficult to distinguish, both being short, extending only 1 mm. or at most 1·5 mm. into the lumen. In places they are so dilated as to be in contact, in others they are fairly thin and the dissepiments between them may be clearly distinguished. No area of

divergence in the septal trabeculæ has been seen. The dissepiments are small and globose but not horse-shoe shaped in vertical section, and are in one or at most two series. The tabulæ are distant, complete and horizontal, or incomplete and forming a depressed floor, the tabellæ being very large and arched.

Remarks. The absence of horse-shoe dissepiments and of an area of divergence in the trabeculæ and the occurrence of a dividing epitheca between the hystero-corallites at increase are important differences from the genotype. Nevertheless the straightness of the corallites and the distant, ragged tabulæ are characteristic of the genus, in which the species is somewhat doubtfully included. A comparison between it and *T. abrogatum* is given in the remarks on the latter. It differs from the only other two known species with equal major and minor septa (two Australian species from the Devonian of Victoria), in the presence of globose and lonsdaleoid rather than horse-shoe dissepiments. Two specimens, F 4312-3, in the University of Queensland collection from Wee Jasper, probably belong to this species.

Family FAVISTELLIDÆ.

Favistellidæ Hill, 1939*b*, p. 240. Range Upper Ordovician to Middle Devonian.

Genus Favistella Hall.

Favistella Hall, 1847, p. 275 ; for references and species see Hill, 1939*b*, p. 241. Range, Upper Ordovician to Middle Devonian.

Genotype. *Favistella stellata* Hall, 1847, p. 275, pl. lxxv, figs. 1*a-c.* Hudson River group (Upper Ordovician), Indiana.

Diagnosis. Compound Rugosa with complete tabulæ and short minor septa, without dissepiments.

Favistella sp.

(Plate X, fig. 6.)

One specimen, F 4293, University of Queensland collection, from the Sponge limestone on the Wee Jasper road about one mile from the Taemas bridge, 1937, is a *Favistella*, although material is too scanty for a complete description. The corallum is fasciculate and small, the corallites diverging. They are 2 to 3 mm. in diameter, and may be in contact, when one retains its cylindrical shape at the expense of the other. The wall is thick,

nearly 0·5 mm., and there are up to 24 thin septa, the 12 minor septa extending about 0·3 mm. beyond the wall, and the 12 major extending unequally towards the axis, but not reaching it ; they may curve towards one of two opposite, longer septa.   The tabulæ are complete, distant and arched, but it is not known whether they are domed or saucered.

The specimen is similar to the fasciculate *F. symbiotica* (Charlesworth, 1914, pl. xxxi, fig. 2) from the Lower Devonian of the Eastern Alps, in size, although Charlesworth states that the 24 septa therein included no minor septa, and that they extended to the axis.   In the arrangement of the septa it somewhat resembles the Givetian *F. vulgaris* (Sochkina, 1936, p. 22) from the north Ural, but this is twice as large as our species and has rather shorter septa.   Sochkina has since (1937, p. 13) recorded this species from the Upper Ludlow of the western Ural, where its corallites are similar in size to those of our specimen.

Genus Vepresiphyllum Etheridge.

Vepresiphyllum Etheridge, 1920, p. 7.

Monotype.   Vepresiphyllum falciforme Etheridge, 1920, p. 7, pl. xv, figs. 3, 4.   Devonian, Goodradigbee R., Por. 6, Par. Goodradigbee, Co. Buccleugh, N.S.W.

Diagnosis.   Massive Rugosa with wavy septa bearing lateral and axial upcurved spines ; without dissepiments, and with concave tabular floors, of complete or incomplete tabulæ.

Remarks.   The rows of lateral spines are parallel to the trabeculæ, that is, directed upwards and inwards, and not parallel to the upper edge of the septum.   Similar septa are found in an undescribed species from the Couvinian of Buchan, a fasciculate species in which some corallites are without dissepiments, and have concave rather distant tabulæ like the genotype of *Vepresiphyllum*, but others have spongophylloid dissepiments and small slightly concave tabulæ.   The Buchan species would appear to be generically the same as *Spongophyllum parvistella* Schlüter from the Couvinian of the Eifel, and so it might be that *Vepresiphyllum* is a member of the Spongophyllidæ as previously interpreted (Hill, 1939a, p. 58).   Nevertheless the absence of dissepiments and the typically complete tabulæ suggest relationship to the Favistellidæ

Hill (1939*b*, p. 240), and the genus is provisionally placed herein. In the Australian Lower Devonian of Loyola there is another massive Favistellid, *Loyolophyllum* Chapman, but this differs from *Vepresiphyllum* in the smooth sides of its septa and in the occasional presence of dissepiments.

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Vepresiphyllum falciforme Etheridge

(Plate X, fig. 7.)
</div>

Vepresiphyllum falciforme Etheridge, 1920, p. 7, pl. xv, figs. 3, 4. Devonian, Goodradigbee R., Por. 6, Par. Goodradigbee, Co. Bucclough.

Type Material. Missing, probably in the Mining Museum, Sydney.

Diagnosis. As for genus.

Description. The corallum is compound, massive, normally subhemispherical. The corallites are polygonal, mainly six-sided, with an average diameter of 2-3 mm. The composite wall between corallites is about 0·25 mm. and is formed by the dilatation of the bases of the septa, a median dark line indicating the actual junction of two corallites. There are on the average 12 major and 12 minor septa, the former extending unequally almost to the axis, and the latter being fairly short. Both orders are rather wavy, and somewhat dilated, and both bear lateral spines, curved upwards or sometimes recurved like a bill hook, arranged in rows which curve upwards and inwards from the wall towards the axial edge of the septum, i.e. parallel to the course of the trabeculæ. The axial edges of the septa are also spinose. In vertical section thin deeply concave plates of irregular curvature are seen, rather distant, usually extending right across the lumen, but occasionally a smaller, arched plate may have its outer edge on the wall, and its inner, lower edge on the tabula below ; or still more occasionally there may be two such plates one above another ; such smaller plates are thought to be incomplete tabulæ, not dissepiments.

Remarks. The specimen used for the description is from the Mining Museum, Sydney, but has no number. It is probably from the Goodradigbee district.

<div align="center">

Family MICTOPHYLLIDÆ.
</div>

Typical Genus. *Mictophyllum* Lang and Smith.

Solitary Rugose corals with numerous septa which may be dilated in the dissepimentarium, particularly in the

young stages, but which are attenuate in the tabularium ; the axial ends of the major septa are arranged about an axial point, not a line, and the intersepta loculi in the tabularium are unequal ; the tabular floors are domed, of tabellæ.

Remarks. This family is taken to include the two genera *Mictophyllum* and *Tortophyllum* Sloss (1939, p. 54, with genotype *Zaphrentis cystica* Winchell, Sloss, *op. cit.*, pl. 11, figs. 1-12), which may indeed be synonymous, and which were proposed in the same month. The former is from the Devonian of Canada, Austria and Australia, and the latter from the Hamilton (Givetian) of America. *Tortophyllum* differs from *Mictophyllum*, described below, in having an axial structure due to reinforcement of the tabular domes at the axis by tabellæ. The relation of this family to others is unknown.

Genus Mictophyllum Lang and Smith.

Mictophyllum Lang and Smith, 1939, p. 155 ; Hill, 1939b, p. 246.

Genotype. *Mictophyllum nobile* Lang and Smith *id.*, pl. iv ; Hill, *id.*, pl. xiii, figs. 8, 9 ; Upper Devonian (Frasnian), Lower Chute, Redknife R., a tributary of the Mackenzie R., N.W. Canada.

Diagnosis. Simple Rugosa with septa at first dilated in the dissepimentarium and thin in the tabularium, later thinning in the dissepimentarium also ; the axial ends of the major septa may have an irregular vortical curvature. The tabulæ are domed and replaced by tabellæ, but may sometimes be sagging. The dissepiments are geniculate and sometimes dilated, the dilatation being continuous with that of the septa, and are small, rather globose and steeply inclined.

Remarks. The genus is known in the Lower Devonian of Austria, the Devonian of Australia, and the Upper Devonian of Canada. *Gyrpophyllum curviseptatum* (Stumm, 1937, pl. 55, fig. 2) from the Couvinian Nevada limestone may well belong to it.

Mictophyllum trochoides sp. nov.
(Plate XI, figs. 7-10.)

Holotype. F 17110, Australian Museum (Dun collection). Lower Middle Devonian, Cavan.

Diagnosis. Large, trochoid *Mictophyllum* with well developed minor septa, both orders of septa being rather thick in the dissepimentarium.

Z—August 7, 1940.

Description.   The corallum is trochoid and rather large, the diameter of the holotype increasing from 22 mm. to 30 mm. in 25 mm. Individuals may attain 45 mm. diameter.   There are 38 to 42 major septa at diameters of from 22 mm. to 45 mm., with alternating minor septa ; both orders are dilated in the dissepimentarium, and in the younger stages the dilatation may be continued over the dissepiments ;   their sides are ragged, and one or two specimens show small lateral spines.   Some septa have ragged internal spaces near their peripheral edges, where also they may be buttressed by lateral dissepiments.   The major septa may extend almost to the axis, unequally, and with unequal interseptal loculi in the tabularium ; they may be vortically rotated in the tabularium, or fairly straight, or irregular.   The minor septa are rather short at first, but in the upper parts of the corallum they may be more than two-thirds the length of the major.   The dissepiments are small and geniculate.   The tabulæ are usually incomplete, forming domed tabular floors, but in parts of the corallum the floors may be sagging.

Remarks.   This species differs from the genotype and resembles *M. cresswelli* (Chapman, Hill, 1939*b*, p. 246) in having well developed minor septa.   It differs from the Lower or Middle Devonian Australian *M. cresswelli* chifley in shape, being trochoid rather than cylindrical, and in having rather less dilatation.   There are several specimens in the University of Queensland collection from the Bluff Limestone, on Clear Hill, Cavan, and on the Wee Jasper road 0·5 mile from the Taemas Bridge (1938).   One specimen in the Australian Museum from Cave Flat (F 37800, AM 2979) is probably this species, although the tabularium is proportionately wider.

Family MYCOPHYLLIDÆ.

Mycophyllidæ Hill, 1940*a*, p. 156.

Genus Pseudamplexus Weissermel

Pseudamplexus Weissermel, 1897, p. 878 ; for references, genotype, etc., see Hill, 1940*a*, p. 157.   Range, Lower and Lower Middle Devonian.

Pseudamplexus princeps (Etheridge).

Tryplasma princeps Etheridge, 1907, p. 97.
Pseudamplexus princeps (Etheridge) Hill and Jones, 1940, p. 185, *q.v.* for references and full description.   Range, ? Lower Devonian.

Pseudamplexus aff. princeps (Etheridge).

Two fragments, F 4294-5, University of Queensland collection, from a limestone one-quarter mile downstream from the first karst on the road from Wee Jasper, Goodradigbee R., N.S.W., differ from the ? Lower Devonian Molong specimens in the greater distinction between major and minor septa, but material is too scanty for certainty on their exact specific position. They appear closer to the Molong specimens than to the Lower Middle Devonian specimens of *Pseudamplexus* from Silverwood described by Hill (1940a, p. 158), as their peripheral stereozone is thin, not thick as in the Silverwood specimens.

Family SPONGOPHYLLIDÆ.

Spongophyllidæ, Hill, 1939a, p. 58.

Genus Grypophyllum Wedekind.

Grypophyllum Wedekind, 1922, p. 13 ; 1925, p. 16 *partim.*

Genotype. By designation, *Grypophyllum denckmanni* Wedekind, 1922, p. 14, figs. 13, 14, Lower Givetian beds of Büchel.

Diagnosis. ? Phaceloid Rugosa with long major septa extending unequally to a narrow axial plane, with minor septa frequently suppressed, and with a rather narrow tabularium of concave tabulæ with an axial depression ; lonsdaleoid dissepiments may occur.

Remarks. It is not clear from Wedekind's descriptions whether the corals are solitary or compound, but the latter appears likely. Wedekind designated *G. denckmanni* as genotype in 1922, but in 1925 named *Cyathophyllum isactis* Frech as genotype. The latter choice is of course invalid. The species described by Wedekind in 1925 as *G. gracile*, *G. normale*, *G. tenue*, *G. regressum*, *G.* sp. and possibly *Leptoinophyllum* sp. appear to me to form a group with *G. denckmanni* while those he figured as *G. isactis* (Frech), *G. schwelmense*, *Loipophyllum rotundum* and *L. acrophylloides* seem to form a second group ; but whether these two groups are congeneric it is difficult to know. Both are Givetian in the Eifel. They have been regarded as possible members of the Spongophyllidæ (Hill, 1939a, p. 59). The species described below as a *Grypophyllum*, while fasciculate, has the morphology of the cerioid *Xystriphyllum*, and like it may perhaps be more closely related to the solitary genus *Acanthophyllum* than

to *Spongophyllum*. Or it may be that the Spongophyllidæ
and the Acanthophyllidæ were derived the one from the
other. In any case one can at present only point out
morphological similarities and differences.

The genus *Lyrielasma* Hill (1939*b*, p. 243) from the
Devonian of Victoria bears the same morphological relation
to the thin septaed *Grypophyllum* of the Givetian as the
Acanthophyllum with dilated septa in the Lower and
Lower Middle Devonian bear to the thin septaed *Acantho-
phyllum* of the Middle Devonian. *Cyathophyllum schucherti*
Swartz from the Keyser member of the Helderberg (Lower
Devonian) may be the earliest species of *Grypophyllum*.

Grypophyllum aggregatum sp. nov.
(Plate X, fig. 8 ; Plate XI, fig. 1.)

Holotype. F 10132 (Australian Museum, pres. 1904, by
Miss Yeo). Lower Middle Devonian Cave limestone, Wee
Jasper, Goodradigbee R.

Diagnosis. Phaceloid *Grypophyllum* with septa slightly
dilated, the minor septa being occasionally lost, and with a
wide tabularium.

Description. The corallum is phaceloid, the individual
corallites being fairly closely spaced, and up to 11 mm. in
longest diameter, being oval rather than circular in section.
The average diameter is about 7 mm., and the individual
corallites are very long. The type of increase is unknown.
There are 23 long major septa extending unequally towards
a short axial plane, straight in the dissepimentarium, but
somewhat irregular, wavy and a little carinate in the
tabularium ; the alternating minor septa extend a little
over half-way to the axis, but in some corallites they are
lost. Both orders are a little and equally thickened, the
dilatation being greatest at the periphery, where it is so
great that a narrow peripheral stereozone is formed about
0·5 mm. wide. The dissepiments are regularly concentric,
and rather large, very steeply inclined and unthickened.
The tabular floors are deeply concave, the tabellæ being
rather irregularly surfaced, lightly domed plates.

Remarks. The species somewhat resembles the *G.
denckmanni* group from the lower Givetian of the Eifel,
but differs in having slightly thicker septa, no observed
lonsdaleoid dissepiments, and a narrower dissepimentarium.
In these characters it appears intermediate between the
G. denckmanni group and *Lyrielasma* from the Devonian of

Lilydale. The internal structure is very similar to that
figured for *Cyathophyllum robustum* Maurer (1885, pl. ii,
fig. 1) from the Lower Middle Devonian Waldgirm lime-
stone, but Maurer describes his species as solitary, while
ours is compound.

Genus **Xystriphyllum** Hill.

Xystriphyllum Hill, 1939a, p. 62 ; 1940a, p. 163.

Genotype. *Cyathophyllum dunstani* Etheridge, 1911, p. 3,
pl. A, figs. 1, 2 ; Douglas Ck., Clermont, Q., Lower Middle
Devonian.

Diagnosis. Cerioid Rugosa with long major septa and
well-developed minor septa, with close, concave tabulæ
and globose dissepiments.

Remarks. The genus is known from the Helderberg
(Lower Devonian) of North America, and the Middle
Devonian of Australia and New Zealand. The morpho-
logical resemblance of individual corallites to *Acantho-
phyllum* is striking, and may indicate some relation between
the Spongophyllidæ in which *Xystriphyllum* is somewhat
doubtfully placed, and the Acanthophyllidæ. Possibly
the genus is represented in the Ludlow of the Urals in the
species referred by Sochkina (1937, pl. xvi, figs. 1, 2) to
Acervularia luxurians Eichwald.

Xystriphyllum mitchelli (Etheridge).
(Plate XI, figs. 2, 3,)

Cyathophyllum mitchelli Etheridge, 1892a, p. 172, pl. xi, figs. 9, 10 ;
pl. xii, fig. 4, Cave Flat, Murrumbidgee R., Lower Middle Devonian.

Lectotype. F 2418, Australian Museum collection, Cave
Flat.

Diagnosis. *Xystriphyllum* with numerous septa, and a
wide tabularium of close tabellæ steeply inclined to the
axis.

Description. The corallum is cerioid, the individual
corallites being four to seven-sided, and unequal, the
average diameter being about 7 mm. ; one corallum from
Wee Jasper has corallites uniformly smaller, about 5 mm.
in diameter. There are 22 major septa at a diameter of
7 mm., 16 in corallites at a diameter of 5 mm.   They extend
to the axis unequally, and are wavy and carinate in the
tabularium.   The minor septa are about half as long as
the major ; they also are a little wavy.   Both orders are
somewhat dilated, and are expanded at their bases to form

a narrow peripheral stereozone. The dissepiments are highly inclined and rather globose, in three or four series. The tabular floors are inversely conical, the tabellæ sloping steeply to the axis, and being very close and thin.

- *Remarks.* The species is very similar to *Xystriphyllum dunstani* (Etheridge) from the ? Upper Couvinian of Clermont, in Queensland, as has already been remarked (Hill, 1939a, p. 63).

Localities. The species has been collected from the Cave limestone at Wee Jasper in addition to the type locality ; it also occurs at Cavan in the Sponge limestone ; in the scarp opposite Taemas house on the north bank of the Murrumbidgee and on the Murrumbidgee R. opposite Dawes (Duffy's).

Family ENTELOPHYLLIDÆ.

Entelophyllidæ Hill, 1940b, p. 410.

Compound Rugosa with long, carinate major septa typically ending at a loose axial structure of incomplete tabulæ, or at an aulos, and with numerous, small, globose dissepiments.

Range. Gotlandian of Europe, Niagaran of America, Upper Silurian of Australia, Lower Devonian of Australia, and Middle Devonian of Australia and America.

Remarks. The genus *Eridophyllum* Edwards and Haime is here included in the family, whose diagnosis and range are therefore extended. The Australian species of *Eridophyllum* described below forms a morphological as well as a time link between the Silurian and Lower Devonian *Entellophyllum* and the Middle Devonian *Eridophyllum*. Some of the carinæ on its septa are xyloid as in *Entellophyllum*, and others are yard-arm as in *Eridophyllum*. Its aulos is not the perfect tube of the genotype of *Eridophyllum*, but is imperfect and suggests derivation from the loose axial structure of *Entellophyllum*. Probably the Carboniferous aulate genus *Aulina* is better referred to the Entellophyllidæ than to the Lithostrotiontidæ as at present.

Genus Eridophyllum Edwards and Haime.

Eridophyllum Edwards and Haime, 1850, p. lxxi ; Smith, 1933, p. 518.

Genotype (by designation). *Eridophyllum seriale* Edwards and Haime, 1850, p. lxxi, renamed and described as *Eridophyllum vernuilanum* Edwards and Haime, 1851,

p. 424, pl. viii, fig. 6. Devonian, Columbus, Ohio. (Columbus limestone, Couvinian.)

Diagnosis. Compound Rugosa with carinate septa and an aulos of septal origin, with tabulæ typically in two horizontal series, and with small, globose dissepiments.

Range. Middle Devonian of America, Australia and New Zealand.

Remarks. The Australian and New Zealand species described below differs from the Couvinian and Givetian species of North America in the occurrence of xyloid as well as yard-arm carinæ, and in the imperfection of the aulos.

Eridophyllum bartrumi Allan.

(Plate XI, figs. 4-6.)

Eridophyllum bartrumi Allan, 1935, p. 4, pl. v, figs. 1-3 ; Middle Devonian, Lankey Gully, Reefton, New Zealand.

Holotype. Three pieces in the Auckland University College collection, and one piece in the British Museum.

Diagnosis. Eridophyllum with xyloid and yard-arm carinæ, and with septal trabeculæ usually discrete, grouped into an imperfect aulos.

Description. The corallum is phaceloid or partly cerioid, individual corallites reaching a diameter of 25 mm., in cerioid parts, and up to 20 mm. in phaceloid parts. The corallites are however very unequal, the average diameter being about 15 mm. Increase is peripheral and parricidal. There are 31 major septa and 31 minor septa at a diameter of 23 mm. Both are rather thick, and have both xyloid and yard-arm carinæ without any regularity. The minor septa extend a little over half-way to the axis, but the major septa proceed further, leaving free a tubular space at the axis of the corallite from 2 to 4 mm. in diameter. There are many discrete septal trabeculæ in the tabularium near the axial ends of the major septa, and in some corallites they are aggregated with projections from the septa to form an imperfect aulos. The major septa are also carinate in the tabularium. The tabulæ are thin and incomplete, forming flat or slightly arched floors, very close together. There is no clear differentiation into inner and outer series as in the genotype. The dissepiments are small and globose, steeply inclined throughout but almost vertical in the innermost series. The outermost series may be rhomboid as in some species of *Entellophyllum.*

Range. The species occurs in the Bluff limestone at Clear Hill near Taemas Bridge, and on the road to Wee Jasper half a mile from the Taemas Bridge over the Murrumbidgee R., N.S.W., as well as on the Goodradigbee R. and in New Zealand. It is Lower Middle Devonian.

Remarks. The species differs from the American *Eridophyllum* in the occurrence of xyloid carinæ in addition to the yard-arm type, and in the imperfection of the aulos, which is outlined by septal trabeculæ instead of the continuous wall of the genotype. Its dissepimentarium suggests a relation to *Entellophyllum*.

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Explanation of Plates.

Plate IX.

Lower Middle Devonian Rugosa from the Murrumbidgee.

All figures approximately × 1·4 diameters.

Acanthophyllum æquiseptatum sp. nov.

Fig. 1. Holotype, F 9577, Australian Museum, Clear Hill, west of Boambolo. *a*, transverse ; *b*, vertical section.

Fig. 2. F 17102, Australian Museum, Cavan. Coll. W. S. Dun. *a*, transverse ; *b*, vertical section.

Acanthophyllum asper sp. nov.

Fig. 3. Holotype, F 4270, University of Queensland, first karst on Cave Flat road from Wee Jasper, Goodradigbee R. *a*, transverse ; *b*, vertical section.

Fig. 4. F 4271, University of Queensland, Wee Jasper. Transverse section.

Acanthophyllum ? *clermontense* (Etheridge).

Fig. 5. F 5658, Australian Museum, Cave Flat. Transverse section AM 716.

Acanthophyllum sp.

Fig. 6. F 4273, University of Queensland, first karst on Cave Flat road from Wee Jasper, Goodradigbee R. *a*, transverse ; *b*, vertical section.

" *Campophyllum* " *recessum* sp. nov.

Fig. 7. Holotype, F 16343, Australian Museum, Devil's Elbow, Murrumbidgee R., W. S. Dun Coll. *a*, *b*, *c*, transverse sections ; *b*, vertical section.

Gen. et sp. indet.

Fig. 8. F 9910, Australian Museum, Cavan, A. J. Shearsby Coll. (308). *a*, transverse ; *b*, vertical section.

Fig. 9. F 9909, Australian Museum, Cavan. A. J. Shearsby Coll. (308) transverse section.

" *Cystiphyllum* " aff. *australe* Etheridge.

Fig. 10. F 17158, Australian Museum, Cavan. W. S. Dun Coll. *a*, transverse ; *b*, vertical section.

Fig. 11. F 9588, Australian Museum, Clear Hill. A. J. Shearsby Coll. (170). *a*, transverse ; *b*, vertical section.

PLATE X.

Lower Middle Devonian Rugosa from the Murrumbidgee.
All figures approximately × 1·4 diameters.

" *Cystiphyllum* " cf. *americanum* Edwards and Haime.

Fig. 1. F 4297, University of Queensland, *Receptaculites* beds, Por. 208, Par. Waroo, Taemas. *a*, transverse ; *b*, vertical section.

Disphyllum gemmiforme (Etheridge).

Fig. 2. F 937, University of Queensland, locality unknown.

Fig. 3. F 4235, University of Queensland, Clear Hill, Cavan. Transverse section.

Thamnophyllum abrogatum sp. nov.

Fig. 4. Holotype, F 4240, University of Queensland. Clear Hill, Cavan. Vertical section.

Thamnophyllum curtum sp. nov.

Fig. 5. Holotype, F 9905, Australian Museum, Cavan. A. J. Shearsby Coll. (306). *a*, transverse ; *b*, vertical section.

Favistella sp.

Fig. 6. F 4293, University of Queensland, Sponge Limestone, Wee Jasper road one mile from Taemas Bridge (1937). Section.

Vepresiphyllum falciforme Etheridge.

Fig. 7. Mining Museum, Sydney. Probably from Goodradigbee R.

Grypophyllum aggregatum sp. nov.

Fig. 8. F 4314, University of Queensland, Wee Jasper. *a*, transverse ; *b*, vertical section.

PLATE XI.

Lower Middle Devonian Rugosa from the Murrumbidgee.
All figures approximately ×1·4 diameters.

Grypophyllum aggregatum sp. nov.

Fig. 1. Holotype, F 10132, Australian Museum, Wee Jasper. *a*, transverse ; *b*, *c*, *d*, vertical sections. A.M. 773.

Xystriphyllum mitchelli (Etheridge).

Fig. 2. Lectotype. F 2418, Australian Museum, Cave Flat. *a*, transverse ; *b*, vertical section. A.M. 40.

Fig. 3. F 4315, University of Queensland, Wee Jasper. *a*, transverse ; *b*, vertical section.

Eridophyllum bartrumi Allan.

Fig. 4. F 17099, Australian Museum, Cavan. Transverse sections.

Fig. 5. F 17154, Australian Museum, Cavan. Vertical section.

Fig. 6. F 9581, Australian Museum, Clear Hill. A. J. Shearsby Coll. (174). Transverse and vertical sections.

Mictophyllum trochoides sp. nov.

Fig. 7. Holotype. F 17110, Australian Museum, Cavan. W. S. Dun Coll. *a*, transverse ; *b*, vertical section.

Fig. 8. F 4221, University of Queensland, Clear Hill. Transverse section.

Fig. 9. F 4222, University of Queensland, Clear Hill. Transverse section.

Fig. 10. F 4260, University of Queensland, Bluff Limestone, Wee Jasper road, 0·5 mile from Taemas Bridge (1937). Vertical section.
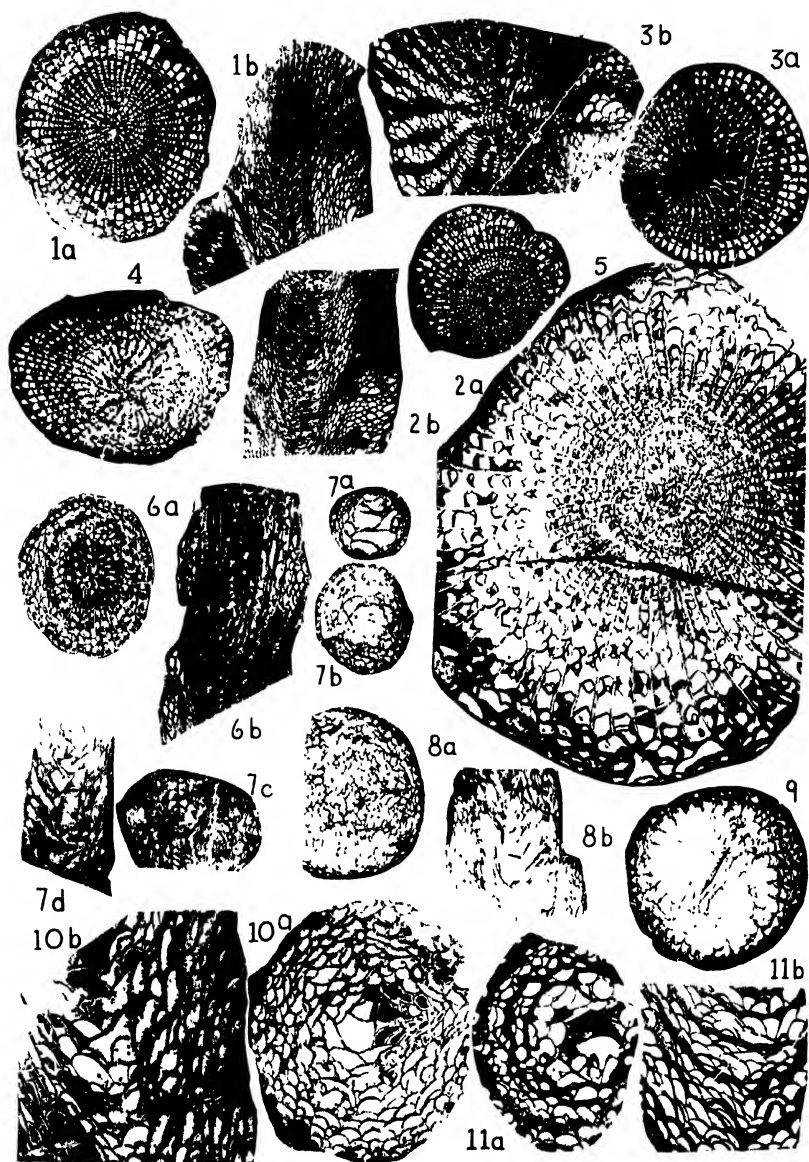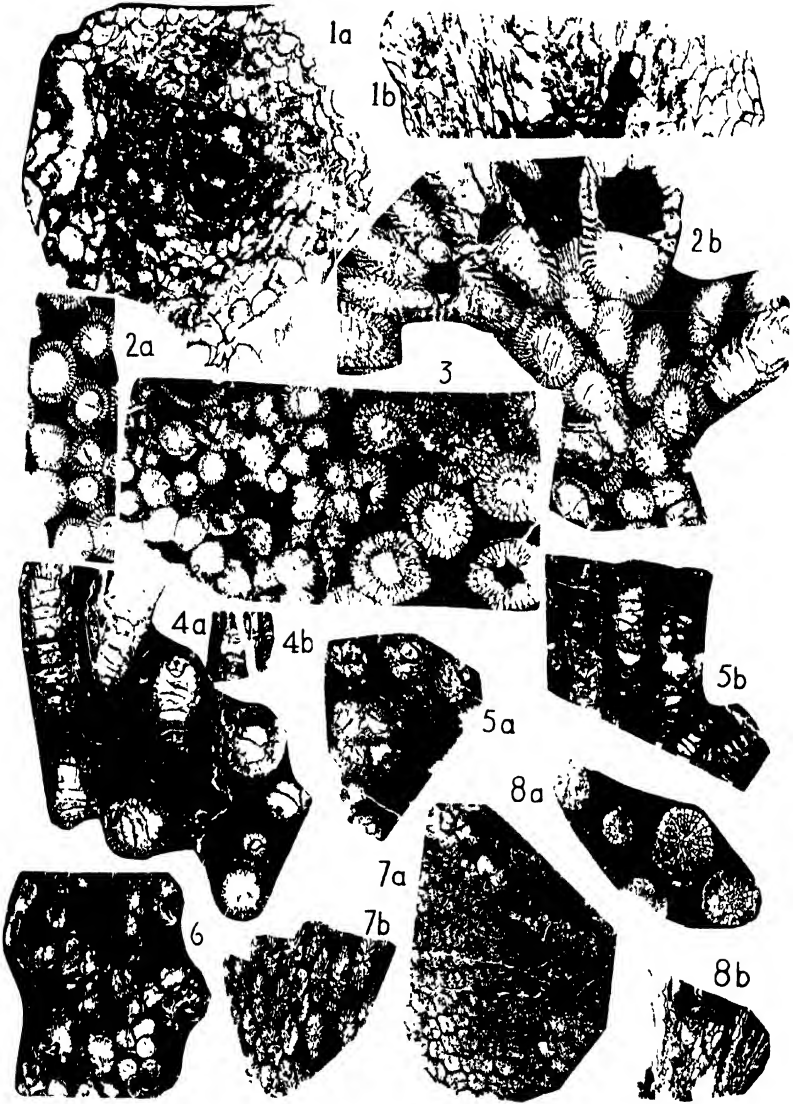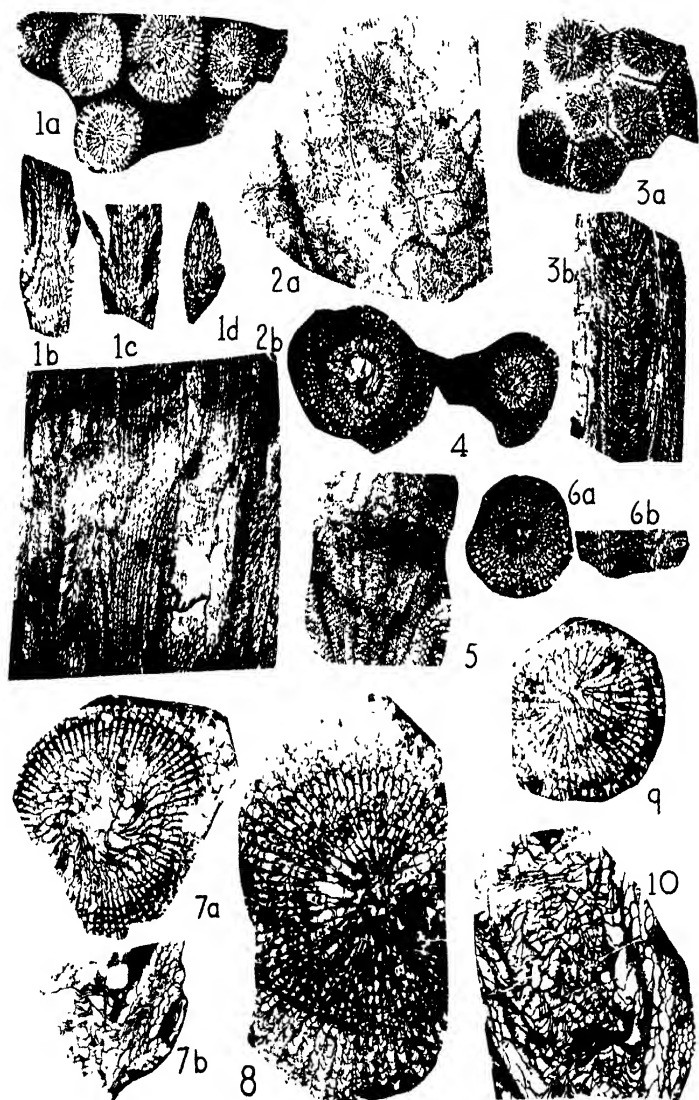
THE ESSENTIAL OILS OF *EUCALYPTUS AUSTRALIANA* (BAKER AND SMITH) AND ITS PHYSIOLOGICAL FORMS.

PART III.

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We are indebted to the Rev. E. Norman McKie of Guyra, New South Wales, for directing our attention, as far back as 1932, to this species growing in the New England district. The leaves and terminal branchlets from which the essential oils were obtained for examination were collected under his personal supervision.

The first consignment of leaves was collected in 1933 from a tree growing seventeen miles east of Guyra on a slate formation at an altitude of over 4,000 feet. The second lot of leaves was forwarded in December, 1936. It was collected from a tree growing on granite country in Paddy's Gully, twenty-three miles north-east of Guyra, at an altitude of 4,000 feet.

The botanical material was identified by botanists as *Eucalyptus australiana* (Baker and Smith), which is synonymous with *Eucalyptus radiata* (Sieber). The leaves and terminal branchlets of the New England trees were found to be similar to botanical material of *Eucalyptus australiana* collected by us at Taggerty in Victoria. Moreover, the essential oils were found to contain similar chemical constituents, but in varying proportions. We have included the result of an examination of the essential oil from a tree growing at Taggerty in Victoria collected in December, 1939, for comparison. The chemical and physical characters of all three essential oils are given in Table I.

We have already discussed the botany of *Eucalyptus australiana* and the chemistry of its essential oil in the

TABLE I.

Locality.	Date.	Weight of Material.	Yield of Oil	$d\frac{15}{15}$	$a_D^{20°}$	$n_D^{20°}$	Piperitone.	Phellandrene.
Guyra, N.S.W.	15. 3.1933	27 lb.	3·9%	0·8950	−43·80°	1·4802	16%	Abundance.
,, ,, ..	16.12.1936	45 lb.	3 0%	0·8988	−44·3°	1·4766	5°/₀	,,
Taggerty, Victoria ..	3. 1.1939	16 lb.	2·7%	0·8886	−63·1°	1·4775	2%	,,

Journal and Proceedings of this Society.* We are unable to classify the variety of *Eucalyptus australiana* from New England and Victoria, as it does not fit into the classification proposed on pages 117 and 118 of the *Journal and Proceedings of the Royal Society of New South Wales*, Vol. LXIX (1935), but for the present we suggest its tentative classification as *Eucalyptus australiana*, Variety " C ".

It is worth noting that as a result of observations extending over many years we sometimes experience difficulty in deciding whether an intermediate form of *Eucalyptus australiana* should be classified as *Eucalyptus australiana* (Baker and Smith) or *Eucalyptus numerosa* (Maiden), so closely does it resemble in morphological characters both these " Narrow-leaved " Peppermints.

The preliminary results of this investigation are deemed worthy of record here, firstly because the New England trees have been under investigation since 1932 and, secondly, because of their economic importance.

The principal constituents which have so far been identified are 1-α-phellandrene, 1-piperitol, 1-piperitone, sesquiterpenes, with a little cymene and unidentified terpene.

EXPERIMENTAL.

Leaves and terminal branchlets of the various consignments, cut as for commercial purposes, were subjected to steam distillation in the usual manner. The chemical and physical constants of the various distillates are given in Table 1.

The respective distillates were subjected to fractional distillation and subsequent detailed examination.

New England, 1933.

100 mls. of crude oil gave the following results on distillation :

Fraction.	Volume.	$d_{15}^{15°}$	$a_D^{20°}$	$n_D^{20°}$
46°– 70° at 10 mm.	41 ml.	0 8525	−62 07°	1·4752
70°– 88° at 10 mm.	8 ml.	0·8795	−41·15°	1·4786
88°–105° at 10 mm.	40 ml.	0·9313	−32 15°	1 4823
Residue	10 ml.			

* Vol. LXIX (1935), pp. 111-122 ; Vol. LXXI (1937), pp. 357-361.

New England, 1936.

100 mls. of crude oil gave the following results on distillation.

Fraction.	Volume.	$d_{\frac{15°}{15}}$	$a_D^{20°}$	$n_D^{20°}$
46°– 70° at 10 mm. ..	44 ml.	0 8496	− 74·07°	1·4766
70°– 80° at 10 mm. ..	11 ml.	0·8926	− 36 57°	1·4785
80°–100° at 10 mm. ..	29 ml.	0·9276	− 30·10°	1 4795
Residue	15 ml.			

Taggerty, Victoria, 1939.

100 mls. of crude oil gave the following results on distillation.

Fraction.	Volume	$d_{15}^{15°}$	$a_D^{20°}$	$n_D^{20°}$
46° 70° at 10 mm.	66 ml.	0 8479	− 76 31"	1 4754
70°– 88° at 10 mm. .	14 ml.	0 8796	− 45 43°	1 4782
88°–100° at 10 mm. .	14 ml.	0 9282	− 29·42°	1 4801
Residue	5 ml.			

Determination of 1-α-Phellandrene.

The terpene fractions distilling below 70° at 10 mm. were fractionally distilled and finally redistilled several times with metallic sodium when the following results were obtained, viz. :

Sample.	Fraction.	Volume.	$d_{\frac{15°}{15}}$	$a_D^{20°}$	$n_D^{20°}$
New England, 1933 ..	Below 60° at 10 mm.	8¼ ml.		− 57·22°	1·4715
,, ,, ,, ..	61°–63° at 10 mm.	22 ml.	0·8486	− 62 4°	1·4770
New England, 1936 ..	Below 60° at 10 mm.	5 ml.		− 74·07°	1·4772
,, ,, ,, ..	61°–63° at 10 mm.	31 ml.	0·8460	− 77·37°	1·4770
Taggerty, Victoria, 1939	Below 60° at 10 mm.	6 ml.		− 73·7°	1·4721
,, ,, ,,	61°–63° at 10 mm.	29 ml.	0·8433	− 84·0°	1·4756
,, ,, ,,	63°–65° at 10 mm.	21 ml.	0·8560	− 76·45°	1·4800

With the limited amount of material available no other terpene could be detected besides phellandrene. The principal fractions distilling at 61°-63° at 10 mm. were treated with maleic anhydride, when the characteristic maleic anhydride adduct was obtained in excellent yield in each case. The three lots of crystals on recrystallisation from methyl alcohol melted at 125° C.

Determination of Piperitol.

The fractions distilling above 90° C. at 10 mm. were freed from accompanying piperitone by treatment with neutral sodium sulphite solution. Subsequent fractionation resulted in the following principal fractions being obtained, viz. :

Sample.	Fraction	Volume	$d_{15}^{15^{\circ}}$	$a_D^{20^{\circ}}$	$n_D^{20^{\circ}}$
New England, 1933 .	91° 98° at 10 mm.	16 ml.	0 9301	- 25 0°	1 4786
New England, 1936 .	94°-98° at 10 mm	18 ml	0 9257	- 32 35°	1 4779
Taggerty, Victoria, 1939	94°-98° at 10 mm.	15 ml.	0 9282	- 29 42°	1·4775

Each fraction was oxidised with Beckman's chromic acid mixture, and the piperitone prepared therefrom purified through the bisulphite compound, using sodium sulphite. The resulting piperitone was identified by the preparation of the α-semicarbazone melting at 225°-226°.

Determination of Piperitone.

This ketone was not present in sufficient quantity to be recovered from either the New England consignment (1936) or the Taggerty, Victoria, lot (1939). As the oil obtained from New England in 1933 contained 16% of this substance, sufficient was isolated for examination. The piperitone thus separated had boiling point 108·5°-110° at 10 mm. and $d_{15}^{15^{\circ}}$ 0·9374, $a_D^{20^{\circ}}$ −21·15°, $n_D^{20^{\circ}}$ 1·4835.

On treatment with excess of hydroxylamine it yielded the characteristic hydroxylamino-oxime of melting point 175°-176°.

Other Constituents.

A search was made for terpinene and terpinen-4-ol, but without success. There were indications of their presence in the oil from Taggerty, Victoria, but confirmation could not be obtained.

ACKNOWLEDGMENT.

Our thanks are due to Mr. D. A. L. Davies of this laboratory for assistance in this investigation.

THE GEOLOGIST AND SUB-SURFACE WATER.*

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I am deeply mindful of the honour conferred upon me by the Society's invitation to deliver this year's Clarke Memorial Lecture.   One difficulty of the lecturer is to select a subject which, while appropriate to the occasion, may be appreciated by those members of the audience who do not profess a knowledge of geology.   The fulfilment or otherwise of this latter condition I must leave to your verdict.

On the other hand there can be little doubt of the appropriateness of the subject on which I speak tonight. The Rev. W. B. Clarke is best known to us for his great pioneering work in the cause of Australian geology, more especially in the field of stratigraphy, and for his observations with respect to the occurrence of gold and of the ores of base metals.   Perhaps few of us realise that he must be honoured also as a pioneer in the local investigation of sub-surface water.

Ninety years ago the problem of water supplies for the growing settlement of Sydney exercised the minds of the community and an attempt was made to test the potentialities of the Hawkesbury sandstone by boring at the gaol. An Artesian Well Board was constituted in 1850, and we learn that the Rev. W. B. Clarke was chairman.[1]

During his diligent explorations in the field he had occasion to record remarks concerning sub-surface waters in some localities.   One example from his writings will suffice to illustrate his interest in the subject.

" In Rock Flat Creek [near Cooma, E.J.K.] there is a remarkable spring of aerated ferruginous water, which bubbles up from below the basaltic rocks, at their junction with the slates.   It was once frequented by people who mixed brandy with it, and spent their time in

* Clarke Memorial Lecture delivered to the Royal Society of New South Wales, June 14, 1940.

[1] Clarke, Rev. W. B.   " Remarks on the Sedimentary Formations of New South Wales ", 4th edition, 1878, p. 72.   Govt. Printer, Sydney.

drinking. A great amount of soda has been deposited by the water. The carbonic acid gas evolved comes up in gushes variable in force and intervals. I found the temperature on 25th November, 1851, on two trials, to be 61 deg. (the air at the time 62 deg.), which is said to be constant summer and winter ; consequently, as the elevation of the spot is 2,736 feet above the sea, this is a warm spring. The water issues through hollows in the tufa, one of which is 3 feet by 2 feet 6 inches, over."[2]

INTRODUCTION.

The controlling importance of water in relation to many of man's activities has been impressed upon the people by the ever-increasing demands for water to meet the needs of growing population and expanding industry. The necessity for systematic records related to quantity, quality, and availability of both surface and sub-surface supplies becomes more pressing each year.

Conservation of surface waters is not always feasible for a number of reasons, such as inadequate rainfall, unsuitable topography, and heavy losses by evaporation and wind action. Recourse must then be had to an alternative source of supply, and, fortunately for man, Nature has provided for his requirements by accumulating within the rocks of the upper portion of the earth's crust waters of such quantities and qualities as permit him to satisfy industrial and domestic requirements.

DEFINITION AND IMPORTANCE OF SUB-SURFACE WATER.

The term sub-surface water is used to designate all water existent within the rocks of the earth as opposed to water present upon the earth's surface or within the atmosphere, whether it be in liquid, solid, or gaseous state.

It is considered that this rock water originated from several different sources, but as regards that portion which is available to man for his use the consensus of opinion among investigators is that it has been derived mainly from precipitation ; that is, from rainfall, snowfall, ice, and sleet. Of these, rainfall is, of course, the most important source.

Geologists regard sub-surface water as a mineral, and, as such, it must be classed as a most important mineral resource to the nation, for there can be no doubt that the valuable pastoral industry could not be pursued within large regions of low rainfall were it not for the fact that

[2] Clarke, Rev. W. B. " Researches in the Southern Goldfields of New South Wales ", p. 170, f.n. Sydney, 1860.

adequate supplies of suitable water are obtainable from the rocks by means of wells and bores. Secondary industries, townships, and irrigation projects are also supplied with water requirements to some extent from sub-surface sources.

UTILISATION OF SUB-SURFACE WATER.

The example set by wild animals possibly taught primitive man to dig for water, and when he learned to domesticate and rear cattle and sheep the well became his most important possession.

Numerous references to the utilisation of water from wells may be found in the Bible. As Meinzer has stated so aptly, " the 26th Chapter of Genesis reads like a water-supply paper ".[3]

Well-known Biblical instances are the Pools of Solomon and Shiloah and Jacob's Well.

History records the Persian origin in the year 800 B.C. of kanats, the most extraordinary works of ancient man for collecting sub-surface water consisting of a network of tunnels connecting the bottoms of shafts. This method was employed in many places, notably in Egypt.

Houses in Athens in the middle of the 6th century B.C. were equipped with deep stone wells, and, before the building of the first aqueduct in 312 B.C., the Romans utilised wells and springs in addition to the water from the Tiber.

There is abundant evidence then that ancient civilisations made great use of " rock reservoirs " for their water needs. Doubtless with the passage of years the ever-increasing demand was met in large measure from sub-surface sources, and wells in great numbers were dug. Obviously depth limitations were governed by sinking methods then in vogue, and only water-bearing formations at relatively shallow horizons could be intersected.

However, in the year A.D. 1126 was witnessed a revolutionary advance in the art of water prospecting, when in the province of Artois in France drilling machinery was developed to test deeper levels and flowing bores were sunk successfully. Hence the origin of the term " artesian water " and of the methods of well-boring which, by continual improvement have played such an essential

[3] Meinzer, O. E. " The History and Development of Ground Water Hydrology ", *Journ. Wash. Acad. Sci.*, 1934. *24*, No. 1, p. 6.

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part in the search for both water and oil throughout the world.

Coming nearer home we find that the stages in the utilisation of sub-surface water are on a par with experience elsewhere, with the possible exception that, as the Australian continent embraces such a large region of relatively low rainfall, the search has been more intense in conformity with the demands of the growth of the pastoral industry.

The aborigines, before the advent of the white man, had drawn water supplies from " soak wells " in the sandy beds of watercourses, and in the very early days of the infant settlement of Sydney the domestic needs of the community were supplemented by wells sunk adjacent to the Tank Stream. Remains of some of these old excavations were disclosed in rebuilding operations of recent years. As the population grew the more pressing became the water supply problem, and in 1850 was constituted the Artesian Water Board, with the Rev. W. B. Clarke as chairman, to which reference has been made above. The object was to bore for artesian water to provide a supply for Sydney, but owing to difficulties encountered in the work and the uncertainty as to ultimate success the enterprise was abandoned without attaining a depth greater than 75 feet.

Small artesian flows of purely local origins have been recorded from the Hawkesbury Sandstone at Gladesville and Redfern, but several bores sunk through this rock and underlying formations in the Sydney district to a maximum depth of 3,000 feet prove that artesian water does not exist here except under the restricted conditions stated.

Naturally the prime consideration in each new settlement and land occupation was the availability of water for domestic purposes and for stock. Suitable surface supplies were not present at every locality, and the settlers were obliged to sink wells at sites which were selected with such success as to suggest the possession of an almost uncanny faculty by the pioneers whose work in testing and proving water-bearing formations throughout the continent should not be forgotten.

Although flowing supplies had been recorded prior to 1880, it was not until this year that an Australian search for artesian water was made on any sound basis following upon a memorable paper presented to this Society by

H. C. Russell,[4] then Government Astronomer, in which he drew attention to the very small discharge by the Darling River of the rainfall received on its catchment, and speculated that a substantial proportion of the rain water must " sink into the ground and flow at some lower level ".

Efforts were crowned with success, and in the intervening years great numbers of bores have been sunk to tap artesian supplies, so that today almost 2,000 flowing bores are in existence within the Queensland and New South Wales limits of the Great Australian Artesian Basin alone.

Shallow-boring for sub-artesian water has received much attention also, particularly in the past 25 years, and many hundreds of bores have been sunk throughout the State to secure water supplies under a variety of conditions of occurrence in rocks of all geological ages.

Government assistance in the search for water is afforded in New South Wales per medium of the Water Conservation and Irrigation Commission. The settler is given the opportunity to meet boring costs by an instalment plan when bores are sunk by plants operated by that authority. During the period 1912-1939 the Commission drilled 3,647 bores, totalling 1,027,133 feet, the average depth being 282 feet. Expenditure exceeded £900,000.

In recent years, especially under drought conditions, the field of activities in water boring has been enhanced appreciably to embrace hitherto unexplored areas in the central and eastern division of our State. Another recent development worthy of mention is the attention focused upon sub-surface supplies for industrial purposes which has led to the exploitation of the resources in sands of the Botany in-fill and in alluvium of the Lower Hunter Valley. Very many bores have been sunk with success to supply requirements for manufacturing processes.

DEVELOPMENT OF INVESTIGATION.

The scientific investigation of the conditions governing the occurrence and availability of sub-surface water is of comparatively recent development. In fact, detailed methods of study are the work of the present century. An understanding of the sciences of geology, meteorology, and hydrology is essential in any properly designed attack upon problems affecting sub-surface water. Of all the

[4] Russell, H. C. " The River Darling—the water which should pass through it ". *Journ. R. Soc. N.S.W.*, 1879, *13*, 169-186.

sciences geology is of the greatest importance, but the necessity for combined effort must not be overlooked. This aspect of the study was stressed by Meinzer, who coined the term " ground-water hydrology " to embrace that branch of the science of hydrology that treats sub-surface water ; its occurrences and motions, its replenishment and depletion ; the properties of rocks that control water movement and storage, and methods of investigation and utilisation.

Superstition enshrouded the earliest concepts with regard to the occurrence of sub-surface water, and the hypotheses of the Greek philosophers chiefly occupied the field until the close of the 17th century, although numerous publications which contained discussions of sub-surface water had appeared from the middle of the 16th century.

The position has been ably summarised by Meinzer in the following words[5] :

" Prior to the latter part of the 17th century it was generally assumed that the water discharged by the springs could not be derived from the rain, first because the rainfall was believed to be inadequate in quantity, and secondly, because the earth was believed to be too impervious to permit penetration of the rain water far below the surface. With these two erroneous postulates lightly assumed, the philosophers devoted their thoughts to devising ingenious hypotheses to account in some other way for the spring and stream water. The two main hypotheses were developed : one to the effect that sea water is conducted through subterranean channels below the mountains and is then purified and raised to the springs : the other to the effect that in the cold dark caverns under the mountains the subterranean atmosphere and perhaps the earth itself are condensed into the moisture which feeds the springs.

" The sea-water hypothesis gave rise to subsidiary hypotheses to explain how the sea water is freed from its salt and how it is elevated to the altitude of the springs. The removal of the salt was ascribed to processes of either distillation or filtration. The elevation of the water was by different writers ascribed to processes of vaporisation and subsequent condensation, to rock pressure, to suction of the wind, to pressure exerted on the sea by the wind and waves, or later to capillary action. One curious explanation was that, owing to the curvature of the earth, the water in the middle of the ocean is actually at a much higher altitude than the springs and hence furnishes the necessary head."

A period of intense activity in artesian well-drilling in France in the first half of the nineteenth century gave a distinct impetus to the study of sub-surface water problems, and in the last half of that century European scientists commenced to record their observations. During this

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[5] Meinzer, O. E. *Loc. cit.*, p. 9.

period may be said to have been laid the foundation of systematic investigation of sub-surface water which led subsequently to the universal recognition of its importance.

Unlike other mineral resources which may be exploited by the individual or by the company for direct profit, and which may receive attention from the mining geologist in private practice or from the academic geologist in his researches, the investigation of sub-surface water as such is practically solely the concern of governmental authorities. Hence we find that the study of the subject today rests mainly with institutions such as official geological surveys and water resources branches. In most countries throughout the world facilities for investigation have been provided and some outstanding organisations have been built up. Perhaps the best example is that of the Division of Water Supply of the United States Geological Survey, with its very numerous publications, which constitute the most comprehensive and most valuable treatment of the subject of sub-surface water, and include contributions by such eminent workers as Meinzer, Slichter, Fuller, and Darton.

Opportunity for exchange of data and for the formulation of universal definitions and standardised methods of investigation is provided today by an organisation known as the International Association of Scientific Hydrology, which includes a Commission on Subterranean Water.

Very little attention appears to have been accorded by Australian geologists to sub-surface water prior to 1880. Again it was the discovery of artesian water which was responsible for awakening interest in the subject. Since that year an extensive bibliography has been accumulated recording the results of very many investigations undertaken by geologists and hydrologists, more especially in the States of Queensland, New South Wales, and South Australia, which each embrace part of that remarkable structural unit known as the Great Australian Artesian Basin.

Perusal of the literature indicates conclusively that the studies were centred very largely upon problems related to artesian basins, their structure, lithology, intake beds, and origin of the water. It is apparent that there has been a tendency to lay particular stress upon the value of artesian water by reason of the large yields obtained from bores, but there can be no doubt that sub-artesian water is of greater importance to the nation as a whole, because it is

distributed far more widely and thus serves the needs of a much larger area and population.

In 1884 a Royal Commission on the Conservation of Water was appointed by the Government of New South Wales " to make a diligent and full inquiry into the best method of conserving the rainfall and of searching for and developing the underground reservoirs supposed to exist in the interior of the colony ". Appreciation of the importance of sub-surface water is implied in this term of reference.

Gradually the realisation arose that the problems of our artesian basins could not be solved satisfactorily without concerted action by all States concerned, and there came into being a series of Interstate Artesian Conferences attended by government geologists, hydrologists, and boring engineers, at which many valuable reports and reviews of extensive data were furnished.

At present a detailed statistical attack upon various aspects of behaviour of water supplies in the Great Artesian Basin is being made by engineers of the Water Conservation and Irrigation Commission of New South Wales and the kindred body in Queensland. This very desirable and excellent work is being undertaken by the respective governments primarily on account of the concern at the persistent diminution in discharge from artesian bores.

It is only within the past thirty years that the systematic investigation of sub-artesian water by Australian geologists has been conducted to any appreciable extent to assess potentialities of water-bearing formations quite apart from flowing supplies. South Australia was early in the field to furnish a series of excellent bulletins of its geological survey.

In 1925 Mr. E. C. Andrews, then Government Geologist of New South Wales, initiated official geological surveys designed for the express purposes of ascertaining resources of all types of sub-surface water in this State, of assisting settlers in the selection of suitable sites for wells and bores, and of cooperation with government and private drillers in the search for water. The project received the whole-hearted support of pastoral organisations and of the Water Conservation and Irrigation Commission.

To date, 71,400 square miles have been mapped by geologists of the Department of Mines, and all available particulars concerning 2,454 wells and bores have been

recorded.   The work is still in progress as opportunity offers.

In addition to these constructive areal examinations, very numerous investigations have been made of proposed sites for bores and wells throughout the State at the request of individual private interests concerned.   Severe and widespread drought conditions prevailing during the past year caused a demand for geological advice as to prospects in excess of all previous levels.   The search for sub-surface water was extended into many parts of the central and eastern divisions of New South Wales hitherto regarded as safe for surface supplies.

The prime objective of official geological work is the assessment of the State's mineral resources.   Sub-surface water ranks high in the list of useful minerals.   It has come to be realised that no geological survey is complete unless it deals with the occurrence and availability of sub-surface water.

Brief Review of Principles of Occurrence.

It is not possible in the compass of a lecture such as this to give more than a brief outline of the general principles governing the occurrence of sub-surface water, but excellent expositions of the fundamental criteria are available in works by Tolman[6] and Meinzer.[7, 8]

Portion of the rain which falls upon the earth's surface finds its way under the influence of gravity into the numerous open spaces or pores associated with the rocks which constitute the upper portion of the earth's crust. These spaces form the receptacles which hold the water that is found below the land surface and is recovered in part through wells and springs.

At the outset it must be realised that the rocks present great variety in composition and structure.   Moreover, their pore spaces differ greatly in size, shape, and arrangement, and, as all these criteria determine the value of formations as water containers, it is obvious that any investigation of the water resources of a region must depend upon a consideration of its geology.

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[6] Tolman, C. F.   " Ground Water ", 8vo, New York, 1937.

[7] Meinzer, O. E.   " Outline of Ground-water Hydrology ", *U.S.G.S. Water Supply Paper* 494.

[8] Meinzer, O. E.   " The Occurrence of Ground-water in the United States, with a discussion of Principles ", *U.S. Geol. Serv. Water Supply Paper* 489.

Given an origin for the water the accumulation of supplies is dependent upon the degree of porosity of the rocks. The more porous the formation the more water will it hold. It does not follow, however, that the more porous rocks will yield the larger supplies, because the quantity of water that a saturated formation will furnish to a well or bore is determined not by its porosity but by its permeability. These two factors are closely inter-related for the reason that the permeability of a rock or its capacity for transmitting water depends largely upon the size, shape, and arrangement of the pore spaces it contains.

There are many different kinds of pore spaces. They may be the interstices or voids between the mineral grains in a sand, gravel, clay, sandstone, or shale ; the cracks, joints and fissures in igneous rocks such as granite, porphyry, and basalt, or in rocks of sedimentary origin such as slate, quartzite, and limestone ; the planes of cleavage and schistosity in slate, gneiss, and schist, especially where such formations are traversed by shear zones ; the partings between the various beds in sediments such as sandstones and shales ; solution channels and cavities produced in limestone and calcareous materials by the solvent action of circulating waters ; or the vesicles and cavities in various types of lava.

The porosity of such rocks as gravel, sand, sandstone, clay or shale is usually uniform and proportionately of a high degree, but, on the other hand, masses of slate and granite may embrace certain zones more fissured, jointed, and cleaved than contiguous units and thus present a wide range of degree of porosity. Some portions of such masses may be practically devoid of interstices.

Before dealing with the question of permeability, consideration must be given to certain forces which control the movement of water. Of these the most important is gravity, for under its influence water percolates from the surface to great depths and laterally for long distances through the pore spaces of the rocks much in the same manner as in any artificial system of water-works with mains and service connections.

But there are other forces which come into operation under certain circumstances and which either restrict the circulation of water or cause water to move contrariwise to gravity. The first-mentioned condition is controlled by the force known as molecular attraction, or the attraction of the walls of the pore spaces for the adjacent molecules'

of water and the attraction of the molecules of water one for another. This force becomes very effective in rocks which have very small pore spaces and results in retention of portion of the contained water. The second phenomenon mentioned is due to the influence of capillarity. If a rock which is ramified by a system of very small interstices is partly immersed in water, the water will be drawn up these pore spaces just as it would creep up gradually in a piece of lump sugar or a biscuit if placed partly in a liquid.

It is apparent then that the permeability of a rock may be restricted by the influences exerted by the forces of molecular attraction and capillarity. Most rocks are more or less permeable to water, but they differ greatly in their degree of permeability according to the number and size of their pore spaces and the extent to which these interstices communicate one with another. In rocks of uniform porosity the yield is least in those which have the smallest pore spaces. For example, a clean gravel may be no more porous than a silt or a clay, yet it may be an excellent source of water, whereas the silt or clay may be worthless because all or nearly all of the contained water in the latter may be held against gravity in the very small interstices by capillarity and molecular attraction.

Again, massive rocks such as granite, limestone, lavas, and slates may possess a low degree of porosity but their pore spaces in the form of joints, cracks, and fissures are large, and hence nearly all the contained water is yielded freely.

Any stratum or rock formation which will furnish an adequate supply of water is termed an " aquifer ". The amount of water which a saturated rock will yield to a well or bore is known as its " specific yield " which, in reality, is a measure of the permeability of the stratum tapped.

According to the conditions under which it occurs sub-surface water may be divided into two major classes, known as

    (1) Ground water.

    (2) Pressure water.

(1) *Ground water* is that which is free and not under pressure exceeding that of the atmosphere at its upper surface. It will not rise when struck in a well or bore, and includes the water present in shallow drifts in the valleys of present-day streams.

(2) *Pressure water* is that which is confined beneath some relatively impervious stratum and which is under pressure exceeding that of the atmosphere at its upper surface. It will rise in wells or bores, and is divisible into two groups :

(*a*) Sub-artesian water.

(*b*) Artesian water.

The difference between these two classes is merely one of degree. Both may be derived from the same aquifer under different conditions of pressure. Sub-artesian water must be lifted to the surface by some artificial means, while artesian water is under sufficient natural pressure to be forced above the surface and flow from bores.

Structure and relationships of rocks play very important parts in the distribution and occurrence of sub-surface water. These considerations are too varied and exhaustive to discuss here.

The Function of the Geologist in Sub-surface Water Investigation.

As it has been demonstrated that accumulation and yield of sub-surface water depend upon such factors as permeability and structure of the rocks, it becomes essential that any programme of investigation designed to determine potentialities should be preceded by a geological survey.

The geologist seeks to establish by field examinations and measurements the extent, thickness, constitution, and structure of the rock formations. He maps the outcrops and by a study of their structural arrangement obtains data as to the probable behaviour of the strata where they may be concealed beneath a cover of other rocks. In this way the attitude, depth, and extent of probable aquifers may be established. Furthermore, mineral constitution of the rocks and position with respect to intake may be used as an index of probable quality of water. Laboratory studies of porosity and permeability, rate of water transmission, and other factors play an important part in the work of both the geologist and the hydrologist.

Cognisance is taken also of the data available from existing bores and wells, especially as to structure and capacity of aquifers in order to assist in attaining a degree of refinement in the investigation so that observations may be applied in unexplored areas with greater accuracy.

It is with respect to this aspect of sub-surface water study that the cooperation of the man on the land, of drillers, and of well-sinkers is invaluable.

Even in this age, phenomena associated with rock water are the objects of superstition and speculation based upon quaint ideas and wild theories handed down from the dawn of history.   It should be the aim of the geologist to counter the air of mystery enveloping the subject by a clear and simple presentation of modern knowledge of occurrence.

WATER-BEARING QUALITIES OF ROCKS, WITH EXAMPLES FROM NEW SOUTH WALES.

Sub-surface water occurs in sedimentary, igneous, and metamorphic rocks, but is present in greatest quantity and widest distribution in the first-mentioned group.

Foremost among the sediments as water-bearing formations are the deposits of sand and gravel in the valleys of our present-day streams.   They possess usually a high degree of permeability and furnish large supplies of good quality waters at shallow depths, a condition of accessibility which brings their exploitation within the means of most settlers.   The more favourable developments are associated with streams in the central and eastern divisions of the State, within, or in proximity to, the Dividing Range which parallels the Pacific coast.   As much as 50,000 gallons per hour are obtainable at individual sites, and several townships, for example Tamworth and Dubbo, are supplied from drift wells.   At Tamworth the average daily consumption in 1938 was of the order of 800,000 gallons, or more than five times the average daily flow from artesian bores in New South Wales.

Beds of sand have an extensive development at shallow horizons beneath areas such as the Western Plains.   These alluvial deposits by reasons of their geographical distribution and of their water-bearing qualities contribute in no mean degree to the needs of the pastoralist and of rural communities.

In the neighbourhood of the City of Sydney a large area of alluvial in-fill with alternating beds of sand and clay occupies an old arm of Botany Bay.   The sands are charged with waters of good qualities utilised mainly for industrial purposes.   Since 1934 at least 50 major production bores have been completed following upon prospecting campaigns involving the sinking of hundreds of test bores.

Individual supplies as high as 20,000 gallons per hour have been proved, in a few instances under artesian pressure. One particular industry uses 100,000 gallons per hour from these sources. Depth to sandstone bedrock is very variable due to great irregularity in profile of the old bay floor, but usually ranges between 60 and 120 feet. The greatest recorded depth of sinking is 250 feet, and as many as eighteen aquifers have been intersected in an individual bore.

Beds of sand and gravel of Tertiary age in ancient stream channels covered by clays and basaltic lava flows, forming what are known as "Deep Leads", are usually heavily charged with water. Originally proved by mining operations for tin and gold, these are being used in some instances today for town supplies and other purposes. The principal examples are found within the central and eastern divisions of the State as at Gulgong, Kiandra, Tingha, and Emmaville.

Important water-bearing formations are the uncompacted Tertiary sands existent at depth in the structure known as the Murray Artesian Basin, of which part is embraced by the south-western portion of the State. The majority of the bores sunk prove sub-artesian conditions, but flowing supplies are evident in several instances. The deepest bore is 1250 feet, and the heaviest flow approximates 200,000 gallons per day. Several aquifers are known and a remarkable feature concerning them is the general decrease in salt content with each successively deeper water. The quantity of saline material and high proportion of purgative salts are so high in any case that the supplies are suitable for stock-watering only.

Sandstones come next in order of value as water containers. Many different types are exposed in New South Wales but the outstanding examples are the friable porous sandstones of Jurassic age which form the intake beds and aquifers of the Great Artesian Basin. This remarkable structural unit has an area of 588,000 square miles, of which 80,000 square miles are within northern New South Wales. The sandstones are exposed extensively along the eastern and south-eastern margins of the Basin and are well exemplified in the region from Warialda to the Queensland border, and from Dubbo to Narrabri, including the Warrumbungle Ranges and Pilliga Scrub region. Moreover, bore logs indicate that the sandstones are present at depth within the Basin resting upon a basement of

Early Palæozoic rocks, mainly slate and granite. The floor of the Basin is modified by irregularities in profile, while the margin is indented by buttresses or promontories of old rocks. According to position in the structure either artesian or sub-artesian water may be obtained.

The waters are of good quality, rarely containing more than half an ounce of total solids per gallon, and are characterised by the presence of sodium carbonate.

The following particulars with respect to the New South Wales portion of the Great Australian Basin, taken from the Annual Report of the Water Conservation and Irrigation Commission for the year ended 30th June, 1939, are quoted as matters of interest :

Total number of bores sunk	763
Number of flowing bores	474
Number of pumping bores	239
Number of failure bores	50
Deepest bore —Boronga	4,338 feet
Largest flow--Yerranbah	1,084,747 galls. per day
Highest temperature—Thurlow Downs No. 2	$140\frac{1}{2}°$ F.
Total flow of all bores	68,652,654 galls. per day

The aggregate flow from all the artesian bores in the Great Australian Basin in Queensland and New South Wales is of the order of 300,000,000 gallons per day. In 1910 the daily flow in New South Wales was gauged at 109,560,972 gallons, but the flow had declined in 1938 to 67,349,317 gallons, although the number of bores increased from 316 to 453 during that period.

Sandstones, silicified sandstones, and quartzites of Devonian age constitute another important group in the central and western divisions of the State occupying an area of approximately 10,000 square miles. The rocks supply water for pastoral purposes from wells and bores ranging in depth from 100 to 800 feet. Supplies as large as 700 gallons per hour are obtained. Quality of the water varies from almost fresh in the outcrop areas to saline water suitable only for stock where the aquifers are intersected beneath younger formations. In many localities the water is stored in numerous joints and cleavages in quartzite rather than in the interstices between individual sand grains.

Solution cavities and openings in limestones offer conditions for the storage and movement of sub-surface water, but relatively small supplies are drawn from these sources in New South Wales, although many exposures of

limestone ranging in age from Pre-Cambrian to Permian are on record.

Coal seams of Jurassic and Permian Ages in the eastern portion of the State furnish small supplies. The water from Jurassic examples is usually carbonated, and in the neighbourhood of Ballimore, near Dubbo, a local artesian basin affords a flow of 2,000 gallons per hour of soda water which has been marketed under the trade name of Zetz Spa.

Igneous rocks are much inferior to sediments as hosts of sub-surface water, although adequate yields for pastoral purposes are being obtained from them in many places. Cracks, fissures, joints, and cavities provide the pore spaces, but the porosity is not uniform in any one mass and is of highest degree in areas of exposure where the rocks have undergone decomposition.

Lava flows, both of Tertiary and Jurassic ages, are the most important members of this group. Such rocks are developed extensively in the Warrumbungle region, and yields as high as 1,000 gallons per hour are being obtained. Large springs also issue at the junction of lava sheets in the Jurassic sequence. Supplies are not potable but are very suited to stock-watering.

Under favourable conditions of decomposition and close-jointing granites may yield excellent water in limited quantities. The mantle of decomposed granite constituting a sandy layer of irregular depths may form a useful aquifer, the downward progress of percolation being arrested by the basement of solid granite. Profile of this bedrock is usually very uneven, so that there is a tendency for water to accumulate in miniature valleys or hollows.

Metamorphic rocks are comparable as water containers with igneous types in the sense that their porosity is determined by the presence of similar structural features. Under certain circumstances slates and cleaved sandstones of Early Palæozoic age yield restricted supplies of useful water in the central division of the State.

In the Broken Hill region considerable attention has been given to the exploitation of the altered Pre-Cambrian rocks for their resources of sub-surface water with very satisfactory results. Many wells yield adequate supplies of good stock water from aquifers provided by such structures as shear-zones, fissures, cracks, jointed zones, schistosity and cleavage planes in rocks comprising schists, gneisses,

slates, amphibolites, and quartzites. While natural conditions are not favourable to the successful conduct of boring operations well-sinking may be relied upon with reasonable prospects.

Concluding Remarks.

From this brief account of the water-bearing potentialities of rocks it will be realised that there is ample scope within our State for the systematic and continued investigation of an asset which is all-important to the man on the land. To date the local study of sub-surface water problems as far as the geologist is concerned has been applied mainly to the qualitative aspect, but it is hoped that the quantitative phase of the work will be gradually developed. For efficient attack it is considered essential that control of investigation of all matters pertaining to accumulation, availability, and utilisation of both surface and sub-surface waters should be centred in one authority, and we may look forward to the day when we possess an organisation as well staffed and endowed as the Division of Water Supply of the United States Geological Survey.

It is only by the co-ordinated efforts of the geologist, the hydrologist, the engineer, the chemist, and the driller that we can hope to achieve results of greater value than those forthcoming today.

In conclusion let me re-echo the sentiments expressed by Mansfield in a recent paper entitled " Geology in everyday life "[9] :

" Geology, through its bearing on supplies of mineral raw materials, necessary adjuncts to our civilisation, enters into many relations of local and national importance. The information it supplies is basic to many great industries. It enters also into more intimate human affairs. Truly it may be said that the relation of human life to geology is as close as that of a fish to water. The earth on which we walk, the air we breathe, the water we drink, the daily events of our lives and even our higher endeavours and aspirations are ordered or affected by geologic phenomena and principles. Though mystery, in the sense of things we cannot explain, enters into geology as it does into life itself, its commoner aspects are so clear, so instructive and so enticing if once sensed, that they can hardly fail to appeal to the imagination and interest of any active mind."

[9] Mansfield, G. R. " Geology in Everyday Life ", *Ann. Rept. Smithsonian Inst.*, Washington, D.C., for year ended 30th June, 1938, p. 273.

ARENACEOUS FORAMINIFERA FROM THE PERMIAN ROCKS OF NEW SOUTH WALES.

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(Communicated by DR. IDA A. BROWN.)

(With Plates XII-XIII.)

Little research has been done on the Permian[2] Foraminifera of Australia since 1905. Extensive collections of rocks of Permian age have been made during the last few years by companies engaged in the search for oil and these have been investigated by the Commonwealth Palæontological Laboratory at Canberra. Numerous Foraminifera, chiefly undescribed, arenaceous species, have been recorded from these collections and an attempt is being made in this paper to describe a few of the more important forms. The specimens are derived from collections from the Hunter River District made by Dr. G. D. Osborne, Dr. H. G. Raggatt and J. N. Montgomery and from Victoria Pass, Mitchell Highway, made by D. Dale Condit for Oil Search Ltd. Some of the species have also been identified from an earlier collection of rocks made in the Hunter River District by Dr. Washington Gray for the Commonwealth Oil Refineries Ltd.

[1] Published by permission of the Minister for the Interior, Canberra.

[2] In 1932 (p. 61) the late Sir Edgeworth David suggested the name "Kamilaroi" for the sequence typically developed in the Hunter Valley, from the base of the Lochinvar Stage to the top of the Upper Coal Measures. There is still difference of opinion in Australia as to what part of the European time scale this sequence should be referred, but the present writers, in common with several other workers, including H. G. Raggatt and H. O. Fletcher (1937 and 1939), believe it to be wholly Permian, the Permian being understood to include the Sakmarian of the Russian Section. Hence the term "Kamilaroi" is considered to be unnecessary. "Permian" is used throughout this paper in the sense given above.

The earliest record of Permian Foraminifera in Australia was in 1882, when the late Professor Rupert Jones discovered tests in some Tasmanian rocks. In 1893 the late Professor Walter Howchin described the first Australian species of this age from the Piper River, N.E. of Launceston, Tasmania. In 1895, Howchin recorded four new species from the so-called Carboniferous of the Irwin River Area, Western Australia. This work, together with that by Chapman and Howchin in 1905 on the Permo-Carboniferous Foraminifera of New South Wales, forms a basis for all later research on the Upper Palæozoic Foraminifera in Australia. The nomenclature used in the last-mentioned publication was revised in 1934 by Chapman, Howchin, and Parr.

The present paper contains the description of one new genus, *Digitina*, four new species, *Ammodiscus multicinctus*, *Ammobaculites woolnoughi*, *Trochammina pulvillus*, and *Digitina recurvata*, one species of *Hyperamminoides* probably referable to an American form, *H. proteus* (Cushman and Waters), and a cosmopolitan form *Textularia eximia* (Eichwald).

All the type specimens are housed in the Commonwealth Palæontological Collection at Canberra.

Family HYPERAMMINIDÆ.

Genus Hyperamminoides Cushman and Waters, 1928.

Hyperamminoides sp. cf. proteus (Cushman and Waters).

Plate XII, Figs. 4 *a*, *b* ; 5 *a-c*.

Cf. *Hyperamminella protea* Cushman and Waters, 1928, p. 36, pl. iv, figs. 5, 6.

Observations.—Cushman and Waters (1928) have described a species of *Hyperamminoides*, under the name of *Hyperamminella protea*, from the Strawn, San Saba County, Texas, U.S.A., which resembles a form common in the Permian of New South Wales. Their description of the species is as follows : '' Test elongate, tapering, the microspheric form very narrow, but regularly increasing in diameter, megalospheric form of nearly uniform diameter for much of its length ; wall of siliceous grains with siliceous cement, smoothly finished on the exterior ; aperture with only a slight constriction. Length, 2·25 mm. ; breadth, 0·30–0·50 mm.''

The New South Wales examples are incomplete, as the proloculum is missing in every case. The initial portion

of both specimens figured by Cushman and Waters is similarly wanting, and it is accordingly not possible to be certain at present that the Australian form is identical with that described from Texas.

The specimens figured are of two types. The first type has a straight, flattened test, slightly tapering towards the initial end, but of nearly uniform diameter for the greater part of its length, thus agreeing with the description given by Cushman and Waters of *H. protea*. Figs. 4 *a, b* on Plate XII represents this type and is comparable with Cushman and Waters' Fig. 6. The second type of specimen is more irregular, being often twisted and transversely corrugated (Pl. XII, Fig. 5 *a, b, c*), but we have no doubt that both forms represent the one species. Distortion without fracture of the fossil shells of arenaceous foraminifera, particularly from shales, is well known and is accepted as due to pressure and movement of the surrounding rock, in view of the fact that living examples of the same genera at no time exhibit the deformation found in the fossil shells.

The New South Wales specimens agree with the description given by Cushman and Waters in having the wall of siliceous sand grains with siliceous cement, smoothly finished on the exterior. They are larger than the Texas specimens, which are stated to be 2·25 mm. long, with a breadth of 0·30–0·50 mm.

Dimensions of Figured Specimens.—Fig. 4, length 3·3 mm., diameter 0·9 mm.; Fig. 5, length 2·8 mm., diameter 1·2 mm.

Occurrence.—Plesiotypes; just below Harper's Hill tuffs, west of Allandale Road turn-off from main Northern Road, near local road to " Oswald " property, Hunter River District, Portion 66, Parish of Greta, County of Durham, Allandale Stage (Comm. Pal. Coll. Nos. 147, 148).

Mulbring Stage.—West half of double railway cutting, west of Minnimbah. Left bank of Hunter River, Long Point, near Singleton, Portion 202, Parish of Darlington, County of Durham. Ascending Box Tree Hill Cutting, Goorangoola Road, north of Singleton, north slope, just over crest of Box Tree Hill, Portion 118, Parish of Broughton, County of Durham. McDougall's Hill, Singleton, Portion 216, Parish of Darlington, County of Durham. One chain west of Padula Siding (Singleton-Muswellbrook Railway), Portion 90, Parish of Darlington, County of Durham. Mt. Thorley, Warkworth Road,

west flank, Loder Dome, Portion 44, Parish of Warkworth, County of Northumberland. John Brown's Reservoir section, south side Mulbring-Buchanan Road, Richmond Vale, by eastern spillway, Portion 10, Parish of Stockrington, County of Northumberland.

Branxton Stage.—Branxton Railway cutting, $\frac{1}{2}$ mile west of Branxton and about 10 chains east of Black Creek (*Fenestella* Beds).

Kulnura Bore, $\frac{3}{4}$ mile south of Kooree Trig. Station, Parish of Kooree, County of Northumberland, from 3,865 feet down to 4,490 feet (?).

Foster's Bridge section, west bank of Mulbring Creek, Portion 9, Parish of Stanford, County of Northumberland. Cutting on railway, west of Pothanna Siding, about 20 feet above *Fenestella* Beds, Portions 51, 52, Parish of Belford, County of Northumberland.

Upper Marine Series.—(Horizon uncertain.) Foot of Victoria Pass, Mitchell Highway, between Mt. Victoria and Hartley.

Farley Stage.—Top of Farley beds, on Farley Road, about 20 chains north-east of Farley Station, Portion 26, Parish of Gosforth, County of Northumberland.

Allandale Stage.—Large railway cutting, about 4 chains west of Farley Station.

Railway cutting, thirty chains west of Farley Railway Station.

About $\frac{1}{2}$ mile S.S.E. of Jackson's Hill, on road along west side of Portion 90, Parish of Pokolbin, County of Northumberland.

Family AMMODISCIDÆ.

Genus **Ammodiscus** Reuss, 1861.

Ammodiscus multicinctus sp. nov.

Plate XII, Fig. 1 *a, b.*

Description of Holotype.—Test planospiral, circular, with parallel sides, consisting of about six whorls, the coiled chamber nearly circular in section, increasing slowly and regularly in diameter and constricted at short, fairly regular intervals, giving a lobulated periphery and undulate surface ; wall moderately thick, coarsely arenaceous, the sand grains cemented with a small proportion of cement giving a roughened surface ; spiral suture distinct ; aperture generally circular, at the end of the tubular chamber.

Dimensions of Holotype.—Diameter, 1 mm. ; thickness, 0·17 mm. Other specimens attain a diameter of 1·8 mm.

Observations.—This species was at first identified as *A. semiconstrictus* Waters, but differs from that form in the close constriction of the spiral tube. Dr. Waters, to whom specimens have been submitted, has also stated that the two forms are distinct. Paalzow (1935) has figured a species, *Ammodiscus bradynus* (Spandel), from the Permian, (Zechstein) of Germany, which somewhat resembles *A. multicinctus.* According to Paalzow *A. bradynus* does not exceed 0·5 mm. in diameter, and his figures show that the shell is not regularly constricted as in the New South Wales form.

Occurrence.—Holotype : large railway cutting about 4 chains west of Farley Station, Hunter River District, Allandale Stage. (Comm. Pal. Coll. No. 149.)

Mulbring Stage.—West half of double railway cutting, west of Minnimbah.

Foster's Bridge section, west bank of Mulbring Creek.

John Brown's Reservoir section, Mulbring-Buchanan Road, Richmond Vale, by eastern spillway. Pelaw Main-Richmond Main railway-line section, Portion 119, Parish of Stockrington, County of Northumberland.

Branxton Stage.—Cutting on railway, west of Pothanna Siding.

Upper Marine Series.—(Horizon uncertain.) At foot of Victoria Pass, Mitchell Highway.

Allandale Stage.—Just below Harper's Hill tuffs, on main Northern Road, west of Allandale turn-off, near local road to " Oswald " property.

Family LITUOLIDÆ.

Genus Ammobaculites Cushman, 1910.

Ammobaculites woolnoughi sp. nov.

Plate XII, Figs. 2 *a*, *b* ; 3 *a*, *b*.

Description of Holotype.—Test crozier-shaped, with the early portion closely coiled and consisting of a single whorl of five to six inflated chambers, the remainder of the test uncoiled, with up to five chambers in a rectilinear series, frequently gradually increasing in size as added ; slightly compressed ; sutures depressed ; wall coarsely arenaceous with a rough surface ; aperture terminal and nearly circular.

Dimensions of Holotype.—Length 1·2 mm., width at apertural end 0·5 mm. Length of paratype, 1·3 mm.,

width 0·6 mm., maximum length of unfigured specimen 2·2 mm., width 0·9 mm.

Observations.—This species is common, but few of the examples show the typical form, as the majority have been laterally flattened or compressed at right angles to the plane of coiling. Immature examples resembling *Haplophragmoides* occur frequently, their identity with the present species being established by the fact that they are invariably associated with it and also that, in some of them the aperture is terminal and not at the base of the final chamber as in *Haplophragmoides.*

The species most nearly resembling *A. woolnoughi* is *A. eiseli* (Spandel), from the Permian (Zechstein) of Germany. This is a comparatively small and smooth-walled species attaining a length of 0·5 to 1 mm., and the rectilinear series of chambers is of uniform width throughout, showing no tendency to flare towards the apertural end of the test. This species is named in honour of Dr. W. G. Woolnough, the Commonwealth Geological Adviser.

Occurrence.—Holotype : Farley Road, 300 yards N.E. of Farley Station, Hunter River District, Farley Stage. (Comm. Pal. Coll. No. 151.) Paratype, same locality. (Comm. Pal. Coll. No. 150.)

Branxton Stage.—Cutting on railway, west of Pothanna siding ; west half of double cutting, west of Minnimbah ; McDougall's Hill, Singleton.

Upper Marine Series.—(Horizon uncertain.) Foot of Victoria Pass, Mitchell Highway.

Farley Stage.—In railway cutting about 12 chains east of Farley Railway Station.

Allandale Stage.—Just below Harper's Hill tuffs, on main northern road, west of Allandale turn-off, near local road to " Oswald " property.

Family Textulariidæ.

Genus Textularia Defrance, 1824.

Textularia eximia (Eichwald).

Plate XIII, Figs. 7 *a-c ;* 8 *a-c.*

Textilaria eximia Eichwald, 1860, p. 355, pl. xxii, figs. 19 *a-d.*

Textularia eximia (Eichwald) Brady, 1876, p. 132, pl. x, figs. 27-29 ; Lange, 1925, p. 237, pl. ii, fig. 36 ; Cushman and Waters, 1930, p. 53, pl. iv, figs. 9-11.

Description of Plesiotype.—Test elongate, tapering, often curved, somewhat compressed with a slight median

groove on each face, margins lobulated; chambers numerous, distinct, as high as wide; sutures almost horizontal, distinct, depressed; wall coarsely arenaceous with little visible cement; aperture a small semi-circular opening at the inner margin of the last-formed chamber.

Dimensions.—Both microspheric and megalospheric forms are represented in our material, the former attaining a length of 1·8 mm. with a breadth of 0·67 mm. The megalospheric form is 1·4 mm. in length, with a breadth of 0·69 mm. Length, according to Brady, 1·7 mm.

Observations.—In all of the specimens from New South Wales the initial end of the test is incomplete. Most of them, while otherwise typical, are more compressed than those figured by Brady from the Carboniferous, apparently as the result of pressure of the enveloping sediments.

Occurrence.—Plesiotypes : railway cutting about 4 chains west of Farley Station, Hunter River District—Allandale Stage (Comm. Pal. Coll. No. 152 microspheric, No. 153 megalospheric).

Mulbring Stage.—West of double cutting, west of Minnimbah.

Upper Marine Series.—(Horizon uncertain.) At foot of Victoria Pass, Mitchell Highway.

Allandale Stage.—Large railway cutting, immediately west of Farley Station, and railway cutting, thirty chains west of Farley Railway Station.

Eichwald described *T. eximia* from the Carboniferous of Russia, where it was associated with Fusulines. Brady's specimens from England and Scotland were also from the Carboniferous. Lange recorded the species from the Middle Permian of Sumatra, while the specimens figured by Cushman and Waters were from the Cisco Group of the Permian in Texas, U.S.A.

Family VERNEUILINIDÆ.

Genus Digitina nov.

Description of Genus.—Test free, elongate, curved, generally almost circular in cross section, early chambers arranged irregularly in the form of a cone, later chambers biserial; wall coarsely arenaceous, consisting of a single layer; interior of chambers undivided; aperture an

arched slit set in a re-entrant angle at the base of the last-formed chamber. Further notes on the genus will be found in the description of the genotype, *Digitina recurvata* sp. nov.

Digitina recurvata sp. nov.

Plate XIII, Figs. 9 *a*, *b* ; 10 *a*, *b*.

Description of Holotype.—The description of the genus applies also to the species.

Dimensions of Holotype.—Length 1·4 mm., diameter 0·6 mm. Length of paratype, 1·6 mm., diameter 0·7 mm. Length of unfigured specimens up to 2·2 mm.

This unusual form recalls the genus *Climacammina* Brady, particularly the genotype, *C. antiqua* (Brady), but differs from it in not developing the terminal uniserial chambers nor a cribrate aperture. The wall in *C. antiqua* is finely arenaceous with calcareous cement, while that of the present species is coarsely arenaceous, the cement being apparently siliceous ; it is not affected by hydrochloric acid. It is probable that the original cement has been replaced, as also seems to be the case in the specimens of *Textularia eximia*.

Brady in his description of *Climacammina* (1876) notes that the genus appears to be related to *Valvulina* rather than to *Lituola* proper or to *Haplophragmium* (these generic names are used in the broad sense, as by Brady), i.e. he considered that they had no affinity with the forms beginning with a planospiral coil in the same plane as the long axis of the test, but that they had a trochoid ancestry. Although Cushman has since placed the genus in the family Textulariidæ, we are inclined to agree with Brady, in view of the similarity of the early stages of his specimens with those from New South Wales. The early portion of the test of *D. recurvata* is almost conical, as Brady found in some young examples of *Climacammina antiqua*. To quote his words " divergence from the *Valvulina*-like mode of growth begins in an uneven or oblique setting on of chambers. But the conical aspect of this part of the test is lost as the Textularian habit is subsequently developed."

The systematic position of *Digitina* is obscure, but it is apparently not textularian, particularly as the early portion is rounded in section throughout. On account of the coarsely arenaceous nature of the shell-wall, it is difficult to make good sections or otherwise determine fully the

structure of the early portion of the test. It can, however, be definitely stated that the chambers in this portion of the shell are often multiple and biserial. Even where they are irregularly biserial, they are added in the form of an elongate spiral until the adult stage of the test is reached.

For the present the genus is placed in the Verneuilinidæ, a family which has not been recorded earlier than the Jurassic. There is a good deal of resemblance between *D. recurvata* and some of the species of *Gaudryina*, particularly the Cretaceous *G. foeda* (Reuss) as recently figured by Cushman (1937).

Occurrence.—Genotype and holotype : at foot of Victoria Pass, Mitchell Highway. Upper Marine Series. (Comm. Pal. Coll. No. 154, paratype No. 155.)

Mulbring Stage.—Minnimbah section, John Brown's Reservoir section, Mulbring-Buchanan Road, Richmond Vale, by eastern spillway.

Branxton Stage.—Foster's Bridge section, west of Mulbring Bridge.

Family TROCHAMMINIDÆ.

Genus Trochammina Parker and Jones, 1859.

Trochammina pulvillus sp. nov.

Plate XII, Fig. 6 *a-c.*

Description of Holotype.—Test small, trochoid, almost circular in outline, the under surface umbilicate, spire low, consisting of about three whorls, the last consisting of six slightly inflated chambers and forming the greater part of the test, sutures straight or a little curved, distinct and depressed ; wall arenaceous, moderately thick, with the surface slightly rough ; aperture narrow, curved at the base of the last-formed chamber and opening into the umbilical depression.

Dimensions of Holotype.—Diameter 0·42 mm. ; height 0·18 mm.

Observations.—*Trochammina pulvillus* is not closely comparable with any previously described species of *Trochammina* with which we are acquainted. A species bearing some resemblance to it is the Recent Arctic form, *T. nitida* Brady, which has a much flatter test, and about nine chambers in the last-formed whorl, but otherwise is of similar build to *T. pulvillus*. *T. arenosa* Cushman and Waters, particularly as figured by these authors from

the Cisco Group of Texas (1930), also has points of resemblance, but has only four chambers to the whorl.

Occurrence.—Holotype: at foot of Victoria Pass, Mitchell Highway. Upper Marine Series. (Comm. Pal. Coll. No. 156.)

Mulbring Stage.—John Brown's Reservoir section, Mulbring-Buchanan Road, Richmond Vale, by eastern spillway.

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Explanation of Plates.

Plate XII.

Fig. 1.—*Ammodiscus multicinctus* sp. nov. Railway cutting immediately
west of Farley Station. Holotype. (*a*) Front view, (*b*) edge
view to show aperture. ×40.

Fig. 2.—*Ammobaculites woolnoughi* sp. nov. Farley Road, 300 yards
N.E. of Farley Station. Paratype. (*a*) Front view, (*b*) apertural
view. ×50.

Fig. 3.—*A. woolnoughi* sp. nov. Locality as above. Holotype.
(*a*) Front view, (*b*) apertural view. ×50.

Fig. 4.—*Hyperamminoides* sp., cf. *proteus* Cushman and Waters. West
of Allandale Road turn-off from main Northern Road, near road
to Oswald property. Plesiotype. (*a*) Front view, (*b*) apertural
view. ×15.

Fig. 5.—*H.* sp., cf. *proteus* Cushman and Waters. Locality as above.
(*a*) Front view, (*b*) side view, (*c*) apertural end. ×15.

Fig. 6.—*Trochammina pulvillus* sp. nov. At foot of Victoria Pass,
Mitchell Highway. Holotype. (*a*) Dorsal view, (*b*) ventral
view, (*c*) side view. ×100.

1a

6c

3a

2a

4b

5a

5b

4a

3b

1b

5c

2b

6a.

J.G-T del

6b.

7a

7b

8a

8b

7c

8c

10b

9a

10a

9b
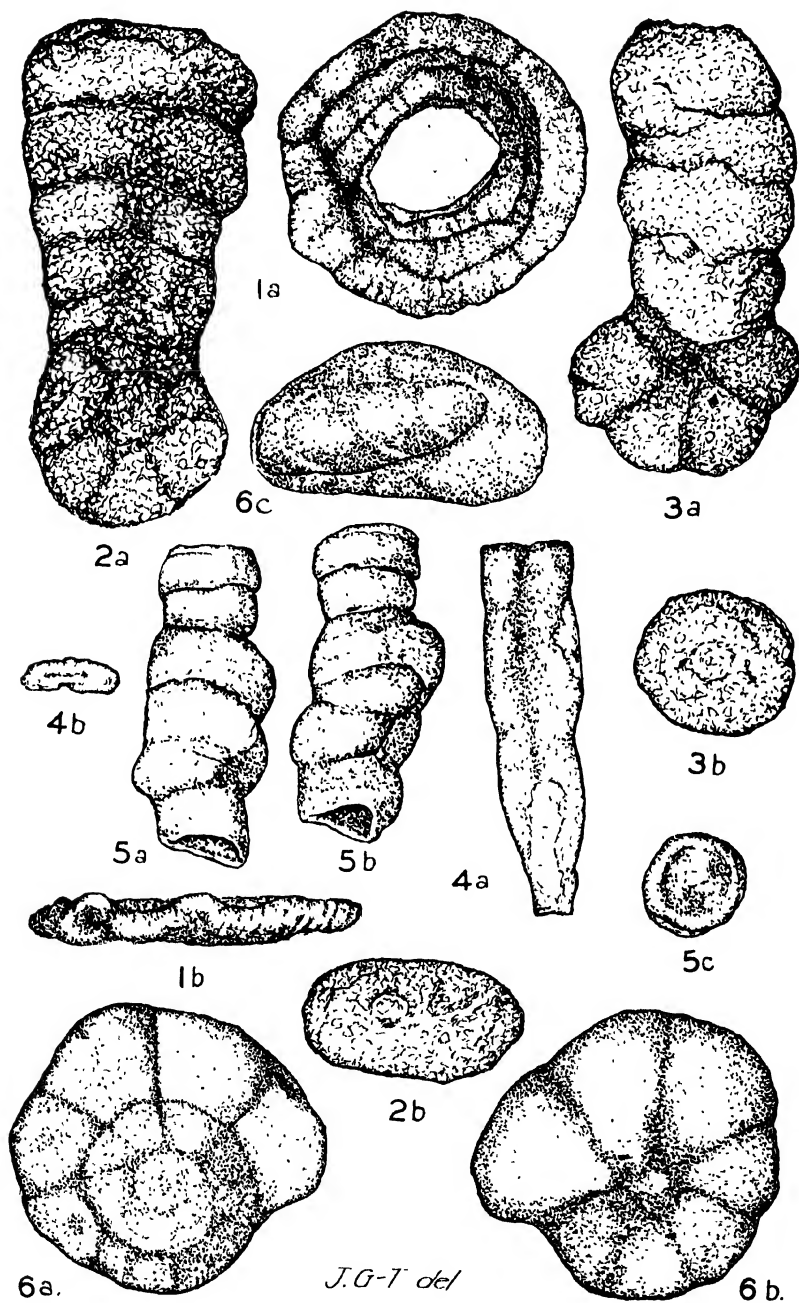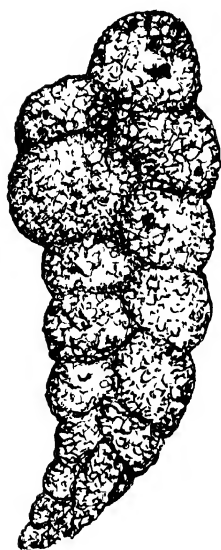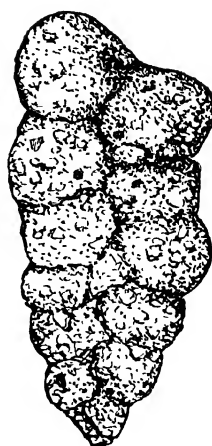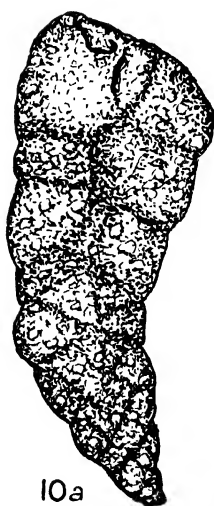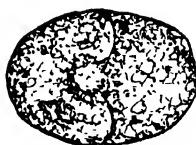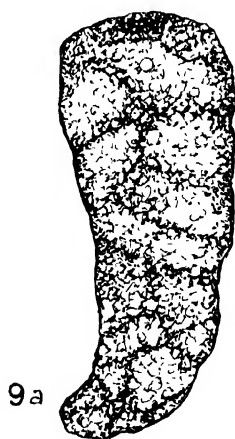
J (i -T del

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PLATE XIII.

Fig. 7.—*Textularia eximia* (Eichwald). Large railway cutting, immediately west of Farley Station. Plesiotype, microspheric form. (*a*) Front view, (*b*) side view, (*c*) apertural view. × 40.

Fig. 8.—*T. eximia* (Eichwald). Locality as above. Megalospheric form. (*a*) Front view. (*b*) side side, (*c*) apertural view. × 40.

Fig. 9.—*Digitina recurvata* sp. nov. At foot of Victoria Pass, Mitchell Highway. Holotype. (*a*) Front view, (*b*) apertural view. × 40.

Fig. 10.—*D. recurvata* sp. nov. Locality as above. Paratype. (*a*) Front view, (*b*) apertural view. × 40.

THE STRATIGRAPHY AND STRUCTURE OF THE SILURIAN AND DEVONIAN ROCKS OF YASS-BOWNING DISTRICT, NEW SOUTH WALES.

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(With Plates XIV-XV.)

CONTENTS.

1. INTRODUCTION AND ACKNOWLEDGMENTS.

The Yass-Murrumbidgee district, situated on the Southern Tableland of New South Wales, about 200 miles south-west of Sydney, is of considerable geological interest inasmuch as strata containing fossils of Silurian and Devonian ages occur in relatively close proximity. Much confusion has existed as to the distribution and structural relations of the two series ever since the examination of the fossil collections of Rev. W. B. Clarke by Salter, who reported (Clarke, 1878, p. 13): "These fossils are of a mixed character, many being of unquestionable Silurian age, and others having all the aspect of Carboniferous and Devonian fossils . . . But if none of the fossils came from

the Carboniferous beds, then there must certainly be Devonian forms mixed with Upper Silurian."

The lack of knowledge of stratigraphical horizon, up to the present, has been due to incomplete geological mapping of the critical areas.

The present investigation was made at the suggestion of Professor L. A. Cotton, to whom the writer is indebted for facilities for carrying out the research. The main objects of this paper are :

(1) To assemble information concerning the stratigraphy and the palæontology of the sedimentary formations near Yass : the bibliography includes all available references, and the list of fossils is believed to contain all recorded forms assigned to their proper stratigraphical horizons ; and (2) to present the results of original field work, and to establish the sequence, structure and geological ages of the sediments in the vicinity of Yass and Bowning.

Much of the accompanying map (Plate XIV) was made in University vacations during the past three years, but it also incorporates the results of other workers. Mr. A. J. Shearsby, of Yass, generously placed his knowledge of the geology of Yass at my disposal and gave every possible assistance. The mapping of the igneous rocks of Bowning Hill was carried out in 1921 by Dr. H. G. Raggatt, who kindly made the results of his work available for publication. The junction of the Laidlaw Series and the Hume Series south of the Yass River was mapped by Mrs. K. M. Sherrard in 1936.

The mapping of the *Dalmanites* (or Middle Trilobite) Bed was carried out by Miss Joan Johnston in 1938. The boundary of the Devonian formations south of the Devil's Pass is taken from the map accompanying L. F. Harper's report (1909) on the geology of the Murrumbidgee Irrigation Area.

On many occasions I have been accompanied by students, particularly Miss J. Gilbert-Tomlinson, B.Sc., and Miss J. Johnston, B.Sc., whose help I gratefully acknowledge.

The expenses of recent field work have been covered by a grant from the Commonwealth Research Fund.

2. Previous Investigation.

The earliest reference to fossils from the district appears to be that of Count P. E. de Strzelecki (1845, pp. 266, 291). Prior to 1844 the Rev. W. B. Clarke (1853, 1860, 1878) had made geological observations in the Yass district, and

had collected fossils which were sent to Europe for identi-
fication by McCoy (1847, p. 228), de Koninck (1876, 1898)
and others. Clarke's specimens described by McCoy are
in the Sedgwick Museum, Cambridge; those described
by de Koninck were returned to Sydney, and were housed
in the Garden Palace in the Botanic Gardens, Sydney,
until its destruction by fire in 1882. Strzelecki's specimens
are in the British Museum (Natural History), South
Kensington, London. The Rugose corals in these collec-
tions were redescribed by Dr. D. Hill (1937).

R. Etheridge's "Catalogue of Australian Fossils"
(1878) refers to previously published records of fossils
from Yass.

The first account of the stratigraphy of the Yass district
is in a paper by C. Jenkins, "On the Geology of Yass
Plains" (1878-1879). Jenkins made extensive collections
of fossils, some of which were described by himself or by
Etheridge. His collections, housed partly in the Australian
Museum and partly in the Department of Geology, Sydney
University, contain much undescribed material, some of
which is being examined by Miss Joan Johnston.

In 1882 Professor Sir T. W. Edgeworth David, then
Geological Surveyor in the Department of Mines, New
South Wales, mapped the area between Hatton's Corner
and Yass.

About this time (1883) J. Mitchell commenced his
researches on the geology and palæontology of Bowning
district, which continued until shortly before his death
in 1928, and to him we owe much of our knowledge of the
Silurian rocks of the Yass-Bowning district. He published
two papers on the general geology of Bowning (1886, 1888),
and numerous papers on the palæontology (chiefly on the
trilobites and brachiopods) both alone and in collaboration
with R. Etheridge, Junr. Etheridge and Mitchell described
and named altogether about 70 new species. These
specimens, as well as much undescribed material, are in the
Australian Museum, Sydney.

Mitchell sent some trilobite specimens to F. Ratte, who
described them in 1886 and 1887; they were later re-
described and named by Etheridge and Mitchell (1896).
A small collection of trilobites and corals from Yass was
sent to A. F. Foerste (1888); these specimens are in the
Smithsonian Institution, U.S. National Museum,
Washington, D.C., and (?) the British Museum (N.H.),
London.

Mr. A. J. Shearsby became interested in Yass geology about 1903, and published descriptions of fossils from 1904 onwards. The operculate corals he described in 1906 are now in the Australian Museum. At the meeting of the A.A.A.S. in 1911 he read a paper on the " Geology of the Yass District ", which was published (1912) with a map and section. The fossils mentioned in this paper were identified by Etheridge, Dun, Chapman, or Shearsby. Some specimens are in the Australian Museum, Sydney, and others are in the National Museum, Melbourne, but not all were preserved.

More recently Mrs. K. M. Sherrard (1936) has made a special study of the rocks of igneous origin. Other references will be found in the bibliography.

3. GENERAL STRATIGRAPHY.
(Plate XIV.)

The oldest formation in the region occurs to the east of Yass and was called by Shearsby (1912) the Jerrawa Shales, since the rocks are typically developed about a railway station of that name. At the time Shearsby regarded these beds as of Silurian age, but Mrs. Sherrard (1939) has examined the Series in more detail and has shown it to be of Upper Ordovician age on the evidence of the graptolites.

Unconformably resting on the Jerrawa Series is a Silurian succession of considerable thickness. This occupies a large area in the vicinity of Yass and Bowning and is highly fossiliferous, especially in the upper portions, with which this paper is particularly concerned.

The Silurian sediments are in turn overlain unconformably in the west and south-west by lavas, which are thought to be Lower or Middle Devonian in age, and outliers of these are found on Bowning Hill.

4. SILURIAN.

Outcrops of Silurian rocks are best seen in shallow sections exposed by the Yass River and its tributaries, since the area has little vertical relief and much of the region is under cultivation or is covered with alluvium. On the map (Plate XIV) these Tertiary (?) and post-Tertiary deposits are not shown, since the main object of the present work is to unravel the structure of the Silurian sequence.

The following descending sequence, based largely on the work of Shearsby and others, has been determined for the Silurian of this area :

Subdivisions.		Nature of the Rocks.	Approximate Thickness.
Hume Series..	..	Limestones, calcareous and tuffaceous shales, sandstones and conglomerates	750'–800'
Laidlaw Series	.	Tuffs and porphyries ..	900'
Yass Series ..	..	Shales, grits, limestones and tuffs . .	800'
Douro Series		Tuffs and porphyry (?)	?
Bango Series	..	Shales and limestones	?
Hawkins Series	..	Tuffs and porphyry (?)	?

Shearsby (1912) recognised the presence of other rocks, alternating with the Bango, Yass, and Hume beds, which he called porphyries and which he and others regarded as intrusive sills. It is now known that, although there may be some igneous rocks among them, they are essentially bedded tuffs, and as such are here incorporated in the stratigraphical sequence as the Hawkins, Douro, and Laidlaw Series, the names being taken from trigonometrical stations situated on ridges formed of the tuffs.

(i) Lithology.

In addition to the series of tuffs mentioned above, which make up more than half the volume of the sediments, the shales, sandstones and grits are composed essentially of finely divided volcanic ash. Even the limestones may contain a large amount of volcanic material; this is especially true of portion of the Bowspring Limestone, the lowest bed in the Hume Series, which, along the Yass River near Hatton's Corner, consists of alternate layers of small limestone boulders and calcareous shaly tuff. The frequent occurrence of siliceous replacements of the fossils in the Bowspring Limestone is evidence of the action of hot springs, following the eruption of huge quantities of volcanic ash, which make up the Laidlaw Series.

There are interesting lateral variations of the sediments, as suggested on the accompanying map. Within the Hume Series limestones and shales have their best development in the eastern and southern portions of the area mapped, and the limestones thin out completely west of the meridian of Bowning Railway Station, their place

being taken by more arenaceous deposits. These changes of lithological facies are accompanied by palæontological variation.

(ii) Tuffs and Porphyry.

Rocks composed essentially of the products of igneous activity were noted first by Jenkins (1878), who described porphyry occurring between the Yass and Hume Beds. In describing the so-called porphyries overlying the Jerrawa Beds, Shearsby (1912, p. 108) states of the lowest (No. 1) porphyry, " This intrusive mass or flow should have careful scrutiny, as in many places it has the appearance of a clastic rock. In the railway cutting near the 183 mile peg it is brecciated and fossiliferous, containing . . . limestone and fossils, such as shell fragments, crinoid ossicles and corals, *Cyathophyllum* and *Favosites*." Similar remarks were applied to the No. 2 (Douro) porphyry.

Columnar jointing occurs in both series. The tuffaceous characters were clearly recognised by Shearsby (1912, pp. 118-119).

The No. 3 porphyry (Laidlaw Tuff) was mentioned by C. Jenkins (1879), partly mapped by T. W. E. David (1882), and described by Shearsby (1912). It has been the subject of closer investigation by Mrs. K. Sherrard (1936). Shearsby recognised tuffs near the lower and upper surfaces, but it was left to Mrs. Sherrard to prove that the greater part of the series was definitely tuffaceous. She recognised a small area of quartz-porphyry along the ridge near Laidlaw Trig. Station ; elsewhere the series consists of tuffs. The rocks belong to the same petrological province, although they vary somewhat in the relative proportions of the minerals present ; the common minerals are quartz, plagioclase (about $Ab_{60}An_{40}$), and chloritised biotite. Unfortunately no detailed chemical investigation of these rocks has yet been attempted.

The mapping of the upper surface of the Laidlaw Series south of the Yass River was carried out by Mrs. Sherrard. The present writer continued the boundary north of the river, from Hatton's Corner northward to Derrengullen (or Barber's) Creek, along the eastern bank of Limestone Creek, then westwards near the Bendenine Road and southwards to the Yass River in the vicinity of Euralie Creek.

As yet no intrusive relations have been shown to occur between the so-called porphyries and the associated

sediments, which are everywhere essentially conformable. Mann's paper (1921) was based on a misinterpretation of the field evidence of a small area south of Yass.

(iii) Bango Series.

These beds were named and described by Shearsby (1912, p. 109), to whose work the reader is referred for details, since no further work has been done on them. They consist of shales and lenticular patches of partly recrystallised limestone, which have weathered down to a broad open valley yielding scanty rock-exposures. Poorly preserved fossils were obtained by Shearsby from the marble quarry north of Coolalie Railway Station. They are quoted in column 1 of the List of Fossils on page 329. Of special interest is the presence of *Halysites pycno-blastoides* Eth. fil., the only known occurrence of this fossil in the Yass district.

(iv) Yass Series.

The Yass beds, named by Jenkins (1879), outcrop in the immediate vicinity of Yass and are well exposed along the banks of the Yass River below the town. This classic section was described by Shearsby (1912, p. 111), who recorded carefully the fossils occurring in the successive bands of sediment. The beds consist of thin-bedded sandstone or grit, possibly tuffaceous, with shales and several thin bands of limestone. The whole series consists of incompetent beds, and has been subject to lateral pressure, causing slight folding with abundant minor faulting, probably before the deposition of the overlying Laidlaw Tuffs. The sediments are of shallow-water origin, and sun-cracks, ripple-marks, and rain-spots are sometimes well preserved, as in Bango Creek under the Hume Highway Bridge.

The Yass Series has been traced by Shearsby northwards to the Wargeilo Road crossing of Derrengullen Creek, with gradual lithological change to tuffs. In Yass Town and southwards to Racecourse Trig. Station four or five thin limestone bands, interbedded with shales, become more conspicuous, striking in a north-westerly direction. This trend is probably due to the influence of the Black Bog Fault, which truncates the series south-east of the town. (See map, Plate XIV.) The Yass Series again occurs on the south side of the fault in O'Brien's Creek, south of the Hume Highway. The beds are again displaced by a dip

fault, so that fossiliferous Yass limestones occur under the Laidlaw Tuffs in Por. 14-22, Par. Hume, due east of Dog Trap turnoff. To the south the beds become more tuffaceous and their further extension is being investigated by Mr. Shearsby at the present time.

On the western side of the syncline fossiliferous shales, which represent the Yass Series, are exposed under tuffs in Bowning Creek, in Por. 59, Par. Bowning, south of the Black Range Road, and also along the railway line and the Binalong Road at the places indicated on the map.

The faunal content is described by Shearsby and a list of the fossils from the Yass Series is quoted in column 2 of Table B, pp. 329-332.

The maximum thickness of the Yass Series is of the order of 800 feet. (See Plate XV, Figs. 1 and 3.)

(v) Hume Series.

This series, also named by Jenkins in 1879, p. 23, and described in part by Mitchell (1886) and Shearsby (1912), overlies the Laidlaw Tuffs and occupies the main portion of the basin shown on the accompanying map.

Jenkins (1879, p. 25) divided this series into "four parts", based on the lithological characters and the faunal content of the beds exposed along the Yass River. His subdivisions are indicated in Table A.

Mitchell worked from the Bowning end of the series, where the lithology is somewhat different from that south of the Yass River. His diagrammatic "Ideal Section of Bowning Synclinal Basin" faithfully represents the surface outcrops of the beds along the line from the junction of Limestone and Barber's (Derrengullen) Creeks on the east and Bowning Creek on the west, although the amounts of dip and the thicknesses of the various beds are much exaggerated. It is to be regretted that Mitchell made no map of the area.

In 1912 Shearsby described the sequence from Yass to Hatton's Corner and beyond in such a way that this section must become a standard of reference for the stratigraphy of the Hume Series. One of the main parts of the present work has been to trace the lateral extensions and variations of the beds recognised in this section and to fix the stratigraphical horizons of the different localities from which the principal fossil collections have been made.

Table A gives a correlation of the horizons recognised by various writers.

TABLE A.

Jenkins, 1879.	Mitchell, 1886.	Shearsby, 1911.	This Paper.	Thickness in Feet.
HUME BEDS.	BOWNING or BOWNYONGIAN BEDS. (n) conglomerate.	HUME BEDS. Bowning conglomerate.	HUME SERIES. tuffaceous conglomerate.	<150
	(m) shale and sandstone.		shale and sandstone.	50 (?)
	(l) upper trilobite bed.	upper trilobite bed.	upper trilobite bed.	<20
Fourth Part.	(k) shale and conglomerate.	conglomerates and shale.	shale and conglomerate.	100
	(j) flaggy sandstone.		Graptolite Bed.	12-20
	(i) conglomerate.		Interbedded shales and conglomerates.	150
	(h) soft shales.			
	(g) conglomerate.			
Phacops Bed.		barren shales.	shales.	100
	(f) great shale bed.	shale with trilobites.	*Dalmanites* bed.	6-10
Third Part		shale.	shale. Black Bog beds.	200
	(e) lower trilobite bed, shale and impure limestone.	limestone.	lower trilobite bed. Hume limestone.	<20 / 0-20
Second Part.	(d) shale.	*Barrandella* shales.	*Barrandella* shales.	5-150
	(c) limestone.	Bowspring limestone.	Bowspring limestone.	0-100
First Part.	(b) grit.	No. 3. PORPHYRY.	LAIDLAW SERIES. grits, etc.	c. 900
	(a) Metamorphic (quartz-porphyry).	Quartz-porphyry tuff.	fine tuffs, coarse tuffs.	.... / ....

In the type section, near Hatton's Corner, and throughout the south-eastern half of the basin, the top portion of the Laidlaw Series consists of fine tuffs. North of Hatton's Corner these tend to be replaced by quartz-grits, which have their maximum development along the north-western margin of the basin, as described by Mitchell. In the neighbourhood of " Euralie ", Yass River, a steeply dipping band of " quartzite " or quartz-grit is interbedded with the fine tuffs.

(a) The overlying *Bowspring Limestone*, so well described by Shearsby for the type-section, has been traced more or less continuously for about 27 miles along the eastern, southern and south-western margins of the Hume Series. The thickness varies from 100 feet at Hatton's Corner to about 50 feet along Derrengullen and Limestone Creeks (where it is richly fossiliferous), until it thins out completely near the Bendenine turn-off from the Booroowa Road. The outcrops are not generally so good south of the Good Hope Road, although west of Reedy Creek and along the Yass River there are fine exposures. Partial (selective) silicification is common throughout the whole of the outcrop of the Bowspring Limestone, corals, brachiopods, and gastropods frequently being replaced.

The faunal content is given in column 3 of Table B. Certain forms are characteristic and distinctive, *Yassia* (*Spongophyllum*) *enormis* (Eth. fil.) being one of the most useful for field work. A large ribbed pentamerid and a gastropod (*Omphalotrochus ? clarkei* de Kon.) are also confined to this zone.

(b) The overlying *Barrandella Shales* (Etheridge, 1904, p. 289) have a lateral distribution similar to that of the Bowspring Limestone. They also appear to have their maximum thickness of about 150 feet at Hatton's Corner and thin out to the north. At Sharpeningstone Creek they are only about 10 feet thick, and farther north only about 5 feet of these shales separate the Bowspring and Hume Limestones. The *Barrandella* Shales are richly fossiliferous (cf. Shearsby, 1911, p. 115) ; a list of the recorded fossils is given in column 4 of Table B, but this is incomplete. *Barrandella linguifer* is widely distributed, *Pisocrinus yassensis* Eth. fil. is abundant in a thin zone, and two cups of *Lecanocrinus breviarticulatus* Chapman have been collected by Shearsby. Corals and other shelly forms are well preserved and abundant.

(c) The *Hume Limestone*, capping the cliff in the Fossil Reserve west of the junction of Booroo Ponds Creek and the Yass River at Hatton's Corner, is 20 feet or less in thickness, but is a persistent bed which is fairly easily mapped ; even where it does not form a scarp its outcrop is readily followed as a rule, for every limestone pebble is a fossil coral. Its approximate position is shown on the map (Plate XIV), on which the thickness of the bed is somewhat exaggerated for the sake of clarity of drawing. This bed of limestone crosses Derrengullen Creek under the railway bridge and follows the western bank of the creek for a couple of miles north. It probably thins out sooner than the Bowspring Limestone, but outcrops are poor. It occurs around the southern portion of the basin, making good outcrops at several places along the Taemas Road as shown on the map. Etheridge's specimens from Old Limekilns Ridge are from this zone. Good outcrops occur at intervals west of Reedy Creek and across the Yass River near Euralie. It thins out completely about a mile north of this point. The recorded Hume Limestone fossils are listed in column 5. The bulk of the fauna consists of Rugose and Tabulate corals. Certain forms like *Mucophyllum crateroides* Eth. fil. and *Zenophila (Phillipsastræa) walli* (Eth. fil.) which do not occur in the Bowspring Limestone are abundant in the Hume Limestone.

(d) *Hume Shales.* Shales immediately overlying the Hume Limestone contain fairly abundant fossils. These shales are well marked along the eastern side of the basin and were recognised by Mitchell also in the north-west and west of Bowning ; they constitute his *Lower Trilobite Bed.* One of Mitchell's chief fossil localities in this zone was in Portions 9, 10, Parish of Bowning (known as Glover's Paddock), in a small tributary of Bowning Creek. A variety of fossils occurs here, notably trilobites (as listed in column 6), brachiopods, and small corals, probably including " *Pleurodictyum* " *megastomum* Dun.

In the south-eastern portion of the Basin the Hume Limestone is succeeded by the Black Bog Shales, which owe their name to their character in wet weather. Fossils are scarce ; a small *Lingula* sp. alone is widespread.

Relatively barren shales, about 200 feet in thickness, overlie the Hume Limestone between Hatton's Corner and Rainbow Hill ; they contain two bands which are more calcareous owing to the presence of trilobites and other shells. These are equivalent to the third part of Jenkins'

Hume Beds, or the lower portion of the Great Shale Bed of Mitchell. Rainbow Hill is capped by a prominent outcrop of calcareous sandstone, the *Dalmanites* Bed (=*Phacops* bed of Jenkins, and Middle Trilobite Bed of Mitchell). This relatively competent bed has resisted weathering, as compared with the associated shales; its outcrop forms low scarps and the shallow dip-slopes it produces probably give a truer indication of the structure of the region than the incompetent shaly beds with which it is associated. A fairly rich fauna has been obtained from this zone, as indicated in column 7. The most abundant forms are trilobites, like *Dalmanites meridianus* Eth. and Mitch., a small Rugose coral, *Streptelasma australe* (Foerste) and numerous small brachiopods. The outcrop of this bed as shown on Plate XIV was mapped by Miss Joan Johnston. Probably the bed formerly covered almost as large an area as the Hume Limestone, but it has not been traced quite so far north. Miss Johnston found it near the Hume Highway Bridge over Derrengullen Creek, and specimens in the Australian Museum come from near the railway bridge on Booroowa Road. South of the Yass River the *Dalmanites* Bed appears to be conformable with the underlying beds. Good exposures occur near the Good Hope Road, along the valley of Reedy Creek and north of the Yass River near Euralie.

The *Dalmanites* Bed is overlain by shales and mudstones of variable thickness containing few if any fossils. This is the upper part of Mitchell's Great Shale Bed. In the bed of a creek in Por. 6, Parish of Yass, west of the junction of the Hume Highway and the Black Range Road, these shales are seen to be almost horizontally bedded; generally the dips are low and in the direction of Bowning Hill. Along Sharpeningstone Creek the shales are succeeded by a series of interbedded shales and thin bands of conglomerate. The exposures elsewhere are poor. These are followed by a bed of tuffaceous sandstone, from 12 to 20 feet in thickness, which in several places contains fragments of plant remains. Owing to its relatively high resistance to weathering, this bed usually forms ridges slightly elevated above the surrounding shaly country. South of the Black Bog Fault its outcrop is almost continuous with that of the faulted *Dalmanites* Bed to the north, and it makes a ridge between this point and the Good Hope Road. To the north it occurs south of the Hume Highway near its junction with Booroowa Road, and runs northward across

Sharpeningstone Creek towards the hill in Por. 34, Parish of Derringullen, on top of which Mrs. Sherrard discovered *Monograptus* spp. (Sherrard and Keble, 1937), also crinoid ossicles and brachiopods in "tuffaceous sandstone". All available evidence indicates that the plant-bearing bed is the same as that containing *Monograptus* spp., although so far the graptolites are known definitely at only the one locality. The specimen of *Monograptus* sp. described by Hall (1904) from Belle Vale probably came from this horizon, although Mitchell regarded it as being from the Lower Trilobite Bed.

Overlying the Graptolite Bed is a series of thin-bedded shales and conglomerates, best exposed in the eastern portion of the basin, along the bed of Sharpeningstone Creek. It was on this exposure that Mitchell based his section east of Bowning Hill. On the western side of the basin in the neighbourhood of Bowning Railway Station, the shales of the Upper Hume Series are locally crumpled and the bedding is difficult to distinguish. The dips along the bedding planes vary from 10 degrees upwards, in an easterly direction. Near the Railway Goods Yard, east of Bowning Station, these beds are overlain by shales containing abundant trilobites, as listed in column 8, and constitute Mitchell's *Upper Trilobite Bed*. They are succeeded by shale and sandstone.

(e) The overlying *tuffaceous conglomerate* appears to be thickest along the eastern limb of the fold and to thin out to the west, where it overlaps on to the fine shales of the Hume Series. A good section is exposed on Bowning Creek, in Por. 113, Parish of Bowning. The southern, eastern and northern foothills of Bowning Hill consist of tuffaceous conglomerate, and outliers were found by Miss Gilbert-Tomlinson over shales about two miles north of Bowning.

The boundaries of the principal bed were mapped by Dr. H. G. Raggatt in 1921. The rock is best exposed at the southern end of Bowning Hill, north of the Black Range Road ; it is not a normal conglomerate but consists of rounded pebbles set in a matrix composed entirely of tuffaceous material, angular fragments of quartz and plagioclase in a fine-grained groundmass. The pebbles are a few inches in diameter and consist of felsites, tuffs, " porphyries " (similar in appearance to various phases of the Bango, Douro and Laidlaw Series), and rounded pebbles of limestone, some of which contain fossils, including

Entelophyllum (*Heliophyllum*) *yassense* (Eth. fil.). This fossil occurs *in situ* only in the lower part of the Hume Series.

The base of the main bed of conglomerate is exposed in a washaway at the side of the road over the northern slope of Bowning Hill. It overlies horizontally-bedded shales, thus disproving Mitchell's hypothetical section showing the base of the conglomerate some 800 feet below the surface. It is probable that the conglomerate does not greatly exceed 150 feet in thickness.

(*f*) *Thickness of the Hume Series.* The thickness of the whole series is shown approximately by the sketch sections illustrated in Plate XV, figures 1, 2 and 3. The thicknesses of the individual beds, as indicated in the last column of Table A, vary from place to place and nowhere does the total thickness approach the sum of the maximum thicknesses of the individual beds.

The field evidence suggests that sedimentation was greatest in the eastern and southern parts of the area ; the beds of limestone and the intervening *Barrandella* Shales thin out to the north and west, their place being taken by sandy beds. This change of facies, lithological and palæontological, is worthy of more detailed investigation.

The maximum thickness of the Hume Series is probably of the order of 750 to 800 feet ; this is considerably less than that indicated by Mitchell (1886) and quoted by Sussmilch (1914).

A test bore put down in 1937 during the construction of the new railway bridge over Derrengullen Creek passed through only 31 feet of limestone and grit before reaching the top of the coarse Laidlaw tuffs. This indicates a general dip of less than two degrees, although the surface dips in this locality are about eight to ten degrees. Thus even the thickness given in this paper may be excessive.

(*g*) *Pyroxene-andesite* or *porphyrite*, called by Shearsby the No. 4 porphyry (1912, p. 119), overlies the tuffaceous conglomerate on Bowning Hill, as illustrated in the sketch-section, Plate XV, fig. 2.

Little work has been done on this formation by the present writer.

The outcrop was mapped by Dr. Raggatt, but further investigation is required as to its mode of occurrence and its petrological and chemical characters. In the field hand specimens are sometimes difficult to distinguish from

the matrix of the tuffaceous conglomerate. Raggatt was unable to obtain conclusive evidence of the origin of the rock, but found that, in Portions 2 and 30, Par. Yass, close to Derrengullen Creek, portions of the matrix of the conglomerate were enclosed in the pyroxene-andesite or porphyrite, which at times shows fluidal structure, suggesting that it was in the form of a volcanic flow.

A good exposure occurs in Bowning Creek, Por. 113, Par. Bowning, showing the tuffaceous conglomerate dipping under the pyroxene-andesite, in conformity with the main structure of the Silurian formations.

The rock is overlain by rhyolites believed to be of Devonian age.

The porphyrite thins out towards the east, as shown in Plate XV, fig. 2, the maximum thickness being about 250 feet.

There is a certain amount of mineralogical variation in a vertical direction, though more work is required here. The rock contains phenocrysts of hypersthene as well as of augite and basic plagioclase, set in a fine-grained groundmass.

The age of the rock is uncertain. It is certainly younger than the tuffaceous conglomerate, but whether it represents the closing phase of Silurian igneous activity or whether it is an interformational sill, remains to be proven. Hypersthene-bearing rocks have not so far been recorded from the Silurian of New South Wales. Shearsby (1912) was in error in linking this rock with the quartz-mica-felspar rock (*Laidlaw Series*) of Harper (1909).

(vi) Geological Structure.

Apparently Mitchell (1886) was the first to recognise that the Bowning beds formed a synclinal structure. Raggatt's work on Bowning Hill confirmed these observations, and Mrs. Sherrard (1936, p. 147) showed that the structure was continued south of the Yass River.

During the course of the present work the complete boundaries of the Hume Series were mapped as shown on Plate XIV, proving that the Series forms a closed basin, elongated in a north-north-westerly and south-south-easterly direction. The underlying Laidlaw and Yass Series are known to form part of the structure, but how much further it extends has not been determined.

The Hume Series outcrops over a length of about seventeen miles and a width of three to four miles. In

general the beds dip towards Bowning Hill, near the centre of the basin. The dips are low at each end of the basin, 5 degrees or less, but slightly greater (averaging 10 degrees) along the eastern portion of the structure. Along part of the western limb of the basin local crumpling has produced some shallow folds, like the flat-topped anticline cut by the Yass River in Portion 148, Parish Warroo, which are separated by steeply-dipping beds. This local folding has caused repetition of the *Dalmanites* Bed.

An examination of the section along the Yass River upstream from Euralie and of the surrounding country shows that the east-west section of the basin is essentially that of a shallow syncline with slight crumpling of the less competent, shaly beds. (Plate XV, fig. 3.)

Contemporaneous movements were responsible for minor faulting in the shales, and later movement produced dip-faults, some of which are shown on the map of the eastern portion of the Hume Series north of the Hume Highway. The majority of these faults have only small amounts of throw, and may die out as monoclinal folds, but, on account of the low dip of the beds, the horizontal displacements of the beds may be relatively great. An oblique fault cutting across Hatton's Creek and displacing the Bowspring Limestone probably continues to the south-east through fine tuffs, where it is difficult to trace. A deposit of ironstone probably indicates its position through the tuffs, and the apparent thickness of the tuffs is increased.

The principal fault (Black Bog Fault) has been traced from near Douro House on the Yass River, $1\frac{1}{2}$ miles east of Yass, in a west-south-westerly direction to Reedy Creek, a distance of five miles. About a mile south of Yass it has a throw of about 400 feet, and causes a displacement of nearly one mile in the outcrops of the Hume Limestone and the *Dalmanites* Bed. The Bowspring Limestone on the northern (upthrow) side of the fault has been subjected to strong shearing, and outcrops as a series of steeply-dipping lenses on the southern slope of the hill west of Racecourse Trig. Station. The fault dies out to the west, and is indicated in Reedy Creek by strong vertical cleavage in the shales, apparently without vertical displacement. The fault is difficult to trace to the east on account of poor outcrops, soil cover and cultivation. The Hume Limestone and the *Barrandella* Shales are thrown against thin-bedded limestones, tuffs and grits of the Yass Series, and further east the Yass Series (on the downthrow side

of the fault) is thrown against the Douro Tuffs, south of Douro House.

About three-quarters of a mile south of this fault is another parallel fault of smaller magnitude, producing a fault-trough. It has thrown Hume Limestone against Bowspring Limestone near the junction of the Taemas and Dog Trap Roads.

In the south-eastern portion of the basin, shallow folding, sometimes nearly parallel to the land-surface, has produced isolated outcrops or inliers of Bowspring Limestone in the *Barrandella* Shales.

(vii) Census and Index of the Fossils.

The accompanying faunal lists have been compiled from all available published records of fossils from the Silurian rocks of the Yass-Bowning district. Fossils from the adjacent Devonian of the Murrumbidgee Valley, between Taemas and Burrinjuck, are not included.

As far as possible each form has been assigned to its appropriate horizon or zone. Mitchell sometimes referred fossils to the Lower Trilobite Bed, which were in shales above or below the Hume Limestone, so that a certain overlap has been inevitable ; also the Graptolite bed is stratigraphically somewhat higher than the *Dalmanites* (Middle Trilobite) Bed, but to simplify the printing, the faunas are grouped together.

The names applied to the fossils do not all have equal value ; some of the fossils have been or are being critically investigated, others hold names which were applied by earlier writers, but which are in need of revision.

The columns numbered 1 to 8 refer to the following horizons :

(1) Bango Series.
(2) Yass Series.
(3) Bowspring Limestone.   ⎫
(4) Barrandella Shales.   ⎪
(5) Hume Limestone.   ⎪
(6) Lower Trilobite Bed.   ⎬ Hume Series.
(7) Middle Trilobite (*Dalmanites*) ⎪
    Bed and Graptolite Bed.   ⎪
(8) Upper Trilobite Bed.   ⎭

The numbers in column 9 refer to the bibliography at the end of the paper.

TABLE B.

Silurian Fossils of Yass District, N.S.W.

	1	2	3	4	5	6	7	8	References.
Porifera—									
Carpospongia sp. ?		x	x	x					82
Ischadites lindströmi Hinde				x					82
"Receptaculites" sp. (= Heliolites sp.)				x					82
Cœlenterata—									
Palæocyclus sp. (= Entelophyllum yassense var.)				x					82
Zaphrentis sp. (= Hercophyllum sp.)..		x		x					82
Amplexus sp. (Tryplasma sp.) ..		x							82
Pycnostylus congregationis (Eth. fil.).				x					82, 39, 54
Pycnostylus dendroides (Eth. fil.) ..			x	x					82, 39, 53, 54
Rhizophyllum interpunctatum de Kon...		x		x					21, 31, 54
Rhizophyllum robustum Shearsby ..		x							82, 81, 54
Rhizophyllum yassense Shearsby ..				x					79, 54
Cystiphyllum sp. cf. bohemicum Pôcta..			x						54
Holmophyllum multiseptatum Hill ..		x							54
Disphyllum præcox Hill..			x	x					54
Mucophyllum crateroides Eth. fil. ..				x	x				82, 34, 54
Murophyllum liliiforme (Eth. fil.) ..			x	x					39, 82, 54
Hercophyllum shearsbyi (Sussmilch) ..		x	x	x	x				87, 82, 61, 54
Bæophyllum colligatum Hill ..			x						54
Tryplasma delicatulum Eth. fil. ..				x					39, 82, 54
T. derrengullenense Eth. fil.				x					39, 82, 54
T. lonsdalei Eth. fil.			x	x					39, 82, 54
Spongophyllum shearsbii Chapman ..			x	x	x				10, 60, 54
S. spongophylloides (Foerste) ..			x	x	x				27, 50, 60, 54
Yassia (Spongophyllum) enormis (Eth. fil.)			x						40, 60, 54
Streptelasma australe (Foerste) ..							x		50, 54
Entelophyllum (Heliophyllum) yassense (Eth. fil.)			x	x	x				32, 61, 54
E. yassense var. patulum (Foerste) ..				x	x	x			50, 54
Zenophila (Phillipsastrœa) walli (Eth. fil.)				x	x				32, 82, 54
Cyathophyllum sp. ..	x								82
Favosites sp.	x								82
Favosites allani Jones . ..			?	x					82, 62
F. gothlandicus forma gothlandica Lamarck			x	x					86, 21, 62
F. libratus Jones			x	x					62
F. richardsi Jones . .			x	x					62
F. regularis Jones			x	x	?				62
F. triporus Walkom			x	x					88, 62
F. yassensis Jones			x	x	x				62
Heliolites sp.	x	x	x	x	x				82
Heliolites daintreei Nich. and Eth. ..			x	x	x				54, 62a
H. distans Dun [– Plasmopora heliolitoides Lindström]					x				25, 62a
H. jackii Dun [= H. daintreei N. and E.]				x	x				25, 62a
H. regularis Dun [– H. daintreei N. and E., etc.] ..				x	x				25, 62a
H. yassensis Dun [– H. daintreei N. and E.]					x				25, 62a
Plasmopora gippslandica (Chapman) .					x				54, 62a
P. heliolitoides Lindström ..			x						54, 62a
P. shearsbyi Dun [– Propora conferta E. and H.]					x				25, 62a
Propora conferta E. and H. ..			x						54, 62a
Hattonia etheridgei Jones				x					59
Coenites spp.			x	x	x				82
C. pinaxoides Eth. fil.		x							41
"Pleurodictyum" problematicum ! ..						x			50
"P." megastomum Dun						x			9, 23
Alveolites spp.		x		x	x				82
A. piriformis Eth. fil.		x		x	x				41
Aulopora sp.		x		x					82

TABLE B.—*Continued.*

Silurian Fossils of Yass District, N.S.W.—Continued.

	1	2	3	4	5	6	7	8	References.
Cœlenterata—*Continued.*									
Syringopora spp.		x		x					82
Halysites pycnoblastoides Eth. fil.	x								82
Stromatoporoid	x	x		x	x				82
Dictyonema sp.							x		85
Dendrograptus sp.				x			?		82
Monograptus spp.							x		51, 84, 85
M. *flemingii* Salter							x		85
M. cf. *tumescens* Wood							x		85
M. cf. *nilssoni* (Barrande)							x		85
M. cf. *vomerinus* (Nicholson).							x		85
Echinodermata—									
Lecanocrinus breviarticulatus Chapm.				x					11
Pisocrinus (?) *yassensis* Eth. fil.				x					82, 38
P. *yassensis* var. *lobata* Eth. fil.				x					37, 82
Stürtzaster mitchelli Eth. fil.								x	36, 78
Palæchinus sp.							x		68
Annelida—									
Spirorbis sp.				x					82
Arabellites bowningensis Eth. fil.				x		x			28, 82
Eunicites mitchelli Eth. fil.				x		x			28, 82
Arenicolites sp.	x	x							82
Œnonites hebes Eth. fil						x			28
Bryozoa—									
Diamesopora sp.				x					82
Fenestella sp		x		x					82
Pinnatopora (*Glauconome*) sp.				x					21,
Ramipora sp.				x					32
Monticulipora sp.		x		x					82
Brachiopoda—									
Lingula sp.						x			82
Orbiculoidea sp.				x					82
Orthis sp.				x					82
O. (*Dalmanella*) *elegantula* Dalman		x		x					82
Stropheodonta spp.				x	x	x			
S. *bendeninensis* Mitchell							x		72
S. *boraeoides* Mitchell				?	?	x	x		72
S. *bowningensis* Mitchell						x	x		72
S. *conica* Mitchell							x		72
S. *davidi* Mitchell							x	x	72, 85
S. *fragilis* Mitchell							x		72
S. *incerta* Mitchell				?	?		x		72
S. (*Brachyprion*) *lihulalensis* Chapman				?		x			72
S. *minuta* Mitchell							x		72
S. *phalænoides* Mitchell						x			72
S. (*Leptostrophia*) *quadrata* Mitchell						x			72
S. *silverdalensis* Mitchell				x					72
S. *striato-costata* Mitchell							x		72
S. *striato-punctata* Mitchell								x	72
S. *transversa* Mitchell						x			72
Orthotetes sp.				x					82
O. *shearsbyi* Dun		x							24, 82
Chonetes spp.		x		x	x				82
C. *melbournensis* Chapman							x		84
C. *bipartita* Chapman							x		84
Pentamerus sp.			x						82
P. *australis* McCoy				x					33
P. *hospes* Barrande (?)				x	?				33
P. (*Barrandina*) *linguifer*				x					82
var. *wilkinsoni* Eth. fil.				x	x		x		33, 3
P. (*Barrandina*) *minor* Booker				x					3
P. *oblongus* Jenkins =P. *australis* McCoy				x					33, 58
P. (*Conchidium*) *knightii*				x					33, 67
P. *pumilis* de Kon.	•			x					21, 33
Sieberella glabra Mitchell sp.				x					82
Rhynchotreta sp.		x							82

TABLE B.—*Continued.*

Silurian Fossils of Yass District, N.S.W.—Continued.

	1	2	3	4	5	6	7	8	References.
Brachiopoda—*Continued.*									
Rhynchonella sp.		x							82
Camarotœchia sp.		x		?					82
Meristella sp.							x		84
Dayia (?) sp.				x					82
Atrypa spp.				x					82
A. reticularis Linn.		x	x	x	x		x		82, 74, 84
A. marginalis Dalman						x			74
A. pulchra Mitchell and Dun						x			74
A. fimbriata ? Chapman							x		85
Atrypoidea australis M. and D.				x					74
A. angusta Mitchell and Dun				x					74
Merista sp.							x		85
Molongia elegans Mitchell				x					71
Retzia salteri Davidson (?)			?						71
Nucleospira australis McCoy							x		85
Spirifer spp.		x		x	x				82
S. plicatella de Kon		x		x					82
S. fimbriata Conrad		x		x					82
S. bowningensis Mitchell							x	x	71
Mollusca									
Ctenodonta sp		x							82
Pterinea laminosa de Kon		x							22, 82
Limoptera ? sp		x							82
Grammysia ? sp		x		x					82
Leptodomus ? sp.				x					82
Orthonota				x					7, 82
Paracyclas sp		x							82
Palæoneilo victorae Chapman				x					82
Modiolopsis ? sp		x							82
Megambonia ? sp		x							82
Chelodes calceoloides Eth. fil.				x					35, 82
Hyolithes sp.		x		x					82
Tentaculites ? sp				x					82
Conularia mitchelli Fletcher								x	49
C. chapmani Fletcher								x	49
C. distincta Fletcher								x	49
Pleurotomaria spp				x	x				82
Murchisonia ? sp		x	x	x					17, 82
Bellerophon ? sp		x		x					18, 82
Euomphalus ? sp				x					82
E. (Omphalotrochus) clarkei de Kon			x						21, 65, 22
Cycloneua sp	x	x		x					82
Loxonema ? sp		x		x	x				82
L. compressa Munster (?)		x							82
Platyceras sp				x					82
Endoceras ? sp. (*Yassia* sp.)									82
Orthoceras sp		x	x	x	x				86, 82
Actinoceras sp.				x					82
Ophidioceras gibbum Chapman				x					11
Spiroceras sp				x					82
Protobactrites sp				x					82
Cyclolituides bowningensis Eth. fil.				x					37
Arthropoda—									
Acidaspis (see *Odontopleura* sp and *Ceratocephala* sp.)									58, 76
Adastocephalum teleotypicum Mitchell								x	70
Bounyonqua (see *Ceratocephala* sp.)								x	48
Bronteus (Goldius) bowningensis E and M								x	48, 30
B. jenkinsi E and M						x			42
B. longispinosus Mitch.						x			66
B. (Goldius) singularis Mitchell						x			73
B. (Goldius) platynotus Mitchell						x			73
Calymene australis E. and M.				x		x	x	x	48
C. duplicata ? Murchison									58
Ceratocephala bowningensis E. and M.						x			48
C. inopedita E. and M.							x		46

TABLE B.—*Continued.*

Silurian Fossils of Yass District, N.S.W.—Continued.

	1	2	3	4	5	6	7	8	References.
Arthropoda—*Continued.*									
C. jackii E. and M.							x		46
C. longispina Mitchell							x	x	67, 46
C. phalærocephala Mitchell ..						x			70
C. vogdesi E. and M.				x		x			46
(= Acidaspis verneuili Ratte non Bar.				x		x			75
or A. vesiculosa Ratte non Beyr.				x		x			75
and A. prevosti Ratte non Barr.) ..				x		x			75
Cheirurus spp.									75, 21
see Crotocephala sp. ..				x		x			57
C. insignis ?									57
Cromus sp.						x			21
see Encrinurus sp.									—
Crotocephalus (Cheirurus) sculptus E. and M...						x			48
C. silverdalensis E. and M. ..						x			48
C. sp.				x					82
Cryptonymus angustus Mitchell ..		x							73
C. incertus Mitchell								x	73
C. perannulatus Mitchell		x							73
C. platynotus Mitchell						x			73
C. robustus Mitchell						x			73
Cyphaspis bowningensis Mitchell ..							x	x	66, 44
C. filmeri Mitchell							x		70
C. horani E. and M.						x	x		44
C. rotunda E. and M.						x			44
C. yassensis E. and M.						x			44
Dalmanites (Hausmannia) loomesi Mitch.							x	x	69
D. meridianus E. and M.							x	x	45
Encrinurus bowningensis Foerste (emen.)				x		x			50, 47
E. etheridgei Mitchell		x							47
E. frontalis Mitchell							x		73
E. mitchelli Foerste			x			x			50, 73
(= ? Cromus murchisoni de Kon. sp.)			,,			,,			21
E. rothwellæ E. and M.								x	47
E. silverdalensis E. and M. ..						x			73
E. spp.		x		x	x				82
Harpes trinucleoides E. and M. ..						x			48
Homalonotus ? sp.						?			58
Odontopleura bowningensis E. and M.					x	x			46, 82
O. jenkinsi E. and M.								x	46
(= Acidaspis brightii Jenkins non Murch.								x	58
= A. prevosti Ratte non Barr.) ..								x	75
Odontopleura parvisimma E. and M. ..						x			46
(= Acidaspis cf. dormitzeri Ratte non Corda)						x			75
Odontopleura rattei E. and M. ..							x	x	46
(= Acidaspis cf. leonhardi Ratte non Barr.)							x	x	75
Phacops crossleii E. and M.								x	45, 82
P. serratus Foerste								x	50, 45
P. latigenalis E. and M.							x		45
P. sp.					x				82
Proetus australis E. and M.						x			43
P. bowningensis Mitchell						x	x	x	66, 43
P. rattei E. and M.						x			43
Sphærexochus miris Beyrich ..				x		x	x		58
Staurocephalus murchisoni Barrande ..									76, 48
Ceratiocaris sp.		x		x					82
Leperditia shearsbii Chapman ..		x							8, 82
Turrilepas mitchelli Eth. fil. ..					x		x		28
Plants—									
Girvanella ? sp.		x							6, 82
Bothotrephis tenuis				x					19, 82

The fossil lists show that a rich and varied fauna occurs in the Silurian sediments of the Yass district, all the principal invertebrate phyla being represented, the most abundant forms being corals, brachiopods, Mollusca, and trilobites.

Foraminifera are so far unrecorded; they have been found by Mr. Shearsby in the Yass Series, and are being examined by him and Mr. F. Chapman.

Porifera are recorded by name only (Shearsby, 1912); sponges are abundant in the shales of Booroo Ponds Creek close to its junction with the Yass River and also in the shales capping the Fossil Bluff of Hume Limestone at Hatton's Corner. The record of *Receptaculites australis* is incorrect; the specimen was probably a weathered specimen of *Heliolites* sp. (verbal communication, A. J. Shearsby). This form has not been found in the Silurian rocks of the Yass district; it occurs only in the Devonian of the Murrumbidgee Valley.

Rugosa have attracted much attention, for they are abundant and well preserved in at least two zones. All known species have been critically examined and the names revised by Dr. Dorothy Hill (1940), so that the list quoted in Table B, pp. 329-332, is complete, and other names previously used are probably incorrect. The massive *Favosites* have also been subjected to revision recently by O. A. Jones (1937).

The **Monograptids** were described and identified by K. M. Sherrard and R. A. Keble (1937) and come from a zone above the Middle Trilobite (*Dalmanites*) Bed.

All species of the **Echinodermata** and **Annelida** found at Yass were described as new to science by Etheridge and Chapman. The genera are known elsewhere.

The **Bryozoa** are in need of critical revision. Fenestellids, including *Pinnaretepora* (*Glauconome*) are not uncommon in the *Barrandella* Shales.

The **Brachiopoda** are abundant and varied; many forms are yet unrecorded. A critical study of these is being made by Miss Joan Johnston. The Stropheodontidæ were named by Mitchell (1923); some of the Pentameridæ by Booker (1926) and the Atrypidæ by Dun and Mitchell.

The **Mollusca** have received little attention. On the whole the specimens are small and poorly preserved. The cephalopoda include two endemic species. The record of *Endoceras* is probably incorrect. Shearsby states (verbal

communication) that it was probably the intrathecal portion of *Yassia* (*Spongophyllum*) *enormis* Eth. fil. Three species of Conularids were described by Fletcher (1938).

The Trilobites form a very important part of the fauna. Sixteen (16) genera, including 48 species, have been recognised.

(viii) Geological Age.

The sediments outcropping in the Yass-Bowning district, the Bango, Yass and Hume Series, appear to form a structural unit : they unconformably overlie the Jerrawa Series containing Upper Ordovician graptolites, and are overlain by Devonian formations.

Thus they represent at least portion of the Silurian System in this region.

The paucity of fossils in the Bango Series and the associated tuffs precludes any exact correlation. *Halysites pycnoblastoides* found in this Series occurs also near Canberra and in the Molong district (Sussmilch, 1914, p. 42) in association with Silurian forms, and is therefore regarded here as an indication of the Silurian age of the Bango Series.

Most of the genera found in the Yass Series occur also in the overlying Hume Series ; these include *Rhizophyllum*, *Hercophyllum*, *Alveolites*, *Atrypa*, *Spirifer*, various Mollusca and Encrinurids. The latter are specifically distinct from Hume forms. This fauna is undoubtedly Silurian.

The most highly fossiliferous beds are in the lower half of the Hume Series ; these contain most of the corals described by Dr. Hill, who considers that this portion of the fauna " represents the top of the Wenlock and perhaps also the base of the Ludlow ". This is in agreement with the earlier work of Etheridge, Dun, and Mitchell.

The crinoid genera *Lecanocrinus* and *Pisocrinus*, and the cephalopod *Ophidioceras*, represented by species in the *Barrandella* Shales, are not known above the Silurian.

The brachiopods include Silurian types of Pentamerids and Strophomenids : the *Atrypa reticularis* is different from the Devonian form.

The Monograptids, *M.* cf. *nilsonni*, *M. flemingi*, etc., occurring above the Middle Trilobite (Dalmanites) Bed, indicate zones equivalent to zones 26 to 33 in the English Silurian sequence, i.e. the top of the Wenlock and the base of the Lower Ludlow.

Possibly the best indicators of the age are the trilobites ; the genera *Ceratocephala*, *Encrinurus*, *Cryptonymus*, *Odontopleura* and *Sphærexochus*—well represented in the Hume Series—are not known to range higher than the Silurian in other parts of the world (Reed, 1928), and the whole assemblage is typically Silurian. Furthermore, four of the above genera, notably the Encrinurids, are well represented in the Upper Trilobite Bed near Bowning Railway Station, the highest fossiliferous bed in the series.

Since the shales pass gradually and conformably into the overlying tuffaceous conglomerate, the latter formation is also included in the Hume Series and the whole is here considered as being of Upper Silurian age.

5. DEVONIAN.

(i) Black Range Series.

Capping the highest parts of Bowning Hill are outcrops of banded rhyolite. The lower surface is almost a plane, which dips slightly to the south of west. Raggatt found that the formation rests partly on tuffaceous conglomerate and partly on pyroxene-andesite. The rock has distinct flow-structure and to the west of Bowning Trig. Station shows columnar jointing, the columns being tilted to the west, approximately at right angles to the base of the flow ; a certain amount of lithological variation occurs and it is probable that several flows are represented. The rock contains small phenocrysts of quartz and albite in a lithoidal groundmass. Partial chemical analyses by H. G. Raggatt and T. J. Hagley showed the presence of from 68 to 71 per cent. SiO_2.

Thus petrographically these rhyolites are distinct from any known rock in the Silurian sequence of this district.

The Bowning rhyolites are regarded as outliers of the series forming the Black Range, a few miles to the west. The latter series may be traced continuously to the south and east, across the Yass River near the Devil's Pass, to the lavas and tuffs of Taemas Hill on the Murrumbidgee River. Here they pass up conformably into fossiliferous tuffs and limestones of Middle Devonian age, and must themselves be regarded as Lower or Middle Devonian. (Harper, 1909.)

The south-westward dip of these tuffs and rhyolites is well exposed on the left bank of Alum Creek between the Devil's Pass and Good Hope, as shown on the south-western portion of the map (Plate XIV).

(ii) Murrumbidgee Series.

Along Alum Creek and southwards to Good Hope, Taemas, and Clear Hill (Cavan) the tuffs and rhyolite of the Black Range Series are conformably overlain by a series of fossiliferous (tuffaceous) shales and limestones. These are thrown into a series of more or less symmetrical folds, whose axes run approximately N. 35° W. and S. 35° E. One of the folds is illustrated by Sussmilch (1914, fig. 19). The shales contain *Spirifer yassensis* de Kon. and the limestones contain a rich and varied fauna. Many forms have been described by Etheridge and others and are listed by Benson (1922, p. 94). The beds have long been regarded as of Middle Devonian age and the recent study of the Rugose corals from some of the limestone by Dr. Hill (1940a) suggests a further limitation of their age to the lower part of the Middle Devonian. These beds, for which the name *Murrumbidgee Series* is proposed, are in need of much more detailed field and palæontological investigation.

6. STRUCTURAL RELATIONS OF THE SILURIAN AND DEVONIAN.

Only brief reference will be made to this subject here, as it is hoped to discuss the matter in more detail in a later paper dealing with the area to the south, in the region of Boambolo, Taemas, and Cavan.

There are, within the area mapped (Plate XIV), sedimentary rocks containing two distinct faunal assemblages, the one Upper Silurian in age, the other lower Middle Devonian. No intermingling of species whatever occurs.

The sediments are separated by products of volcanic activity, which occurred either during Lower Devonian time or at the beginning of the Middle Devonian.

The folding of the Silurian system, apparently deposited on a more or less rigid basement of highly folded Ordovician rocks, is much less pronounced that that of the Middle Devonian beds, and the directions of the fold-axes in the two systems are discordant.

The mapping of the boundary between the two systems as indicated on Plate XIV shows clearly that unconformity exists between the Silurian and Devonian in this region, since the base of the Devonian lavas transgresses successively the eroded surfaces of the Douro, Yass, Laidlaw, and Hume Series, which are dipping in the opposite direction.

It is interesting to find that the palæontological and structural break between the Silurian and Devonian of the region was recognised in the first paper on the geology of the district, that of Jenkins in 1878—over 60 years ago !

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338   IDA A. BROWN.

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To Bendinine

Grits

Grits

Creek

Bowning

Railway

To Albury

Laidlaw Series

Mitchell's Creek

To Binalong

Trilobites

Shales

Yass Series

1807

BOWNING

Hume Highway

To Albury

Quartzite

Shales

Sheep

Grits
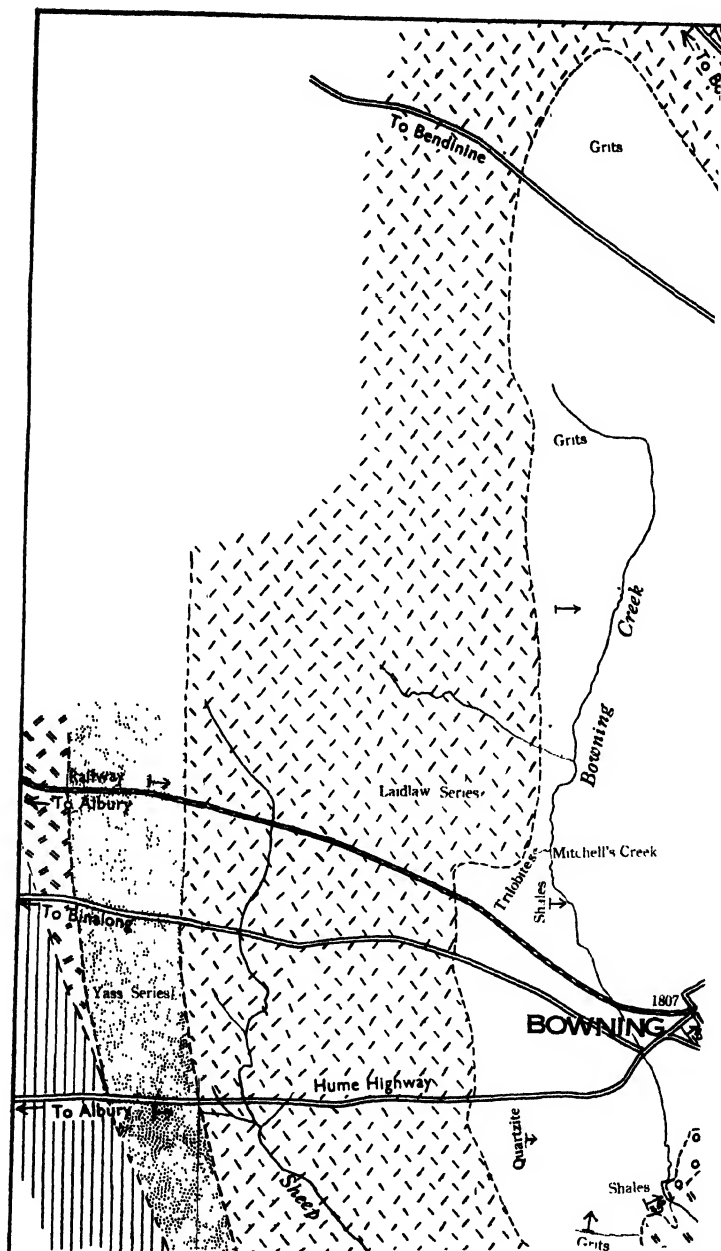
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EXPLANATION OF PLATES.

PLATE XIV.

Geological sketch-map of the Yass District, showing Palæozoic formations (only).

PLATE XV.

Fig. 1.—Generalised east-west section through Ordovician, Silurian and Devonian of Yass District.

Fig. 2.—East-west section through Bowning Hill.

Fig. 3.—Section of Silurian sediments along the Yass River.

RADIAL HEAT FLOW IN CIRCULAR CYLINDERS WITH A GENERAL BOUNDARY CONDITION.

By J. C. JAEGER, B.Sc., M.A.

(Communicated by Professor H. S. Carslaw.)

1. The object of this paper is to give a complete collection of results on radial heat flow in solids bounded internally or externally by circular cylinders with the boundary condition

$$k_1\frac{\partial v}{\partial t}+k_2\frac{\partial v}{\partial r}+k_3v=k_4 \quad \dots\dots\dots\dots\dots \quad (1)$$

at a surface. This boundary condition is more general than those usual in the theory of conduction of heat and includes a large number of cases of practical importance. Some of these are illustrated in § 7 ; it is proposed subsequently to make a numerical study of some problems of this type which are of engineering interest.

It will in all cases be assumed that the constants k have values arising from a physical problem of these types ; if the k are arbitrarily chosen, terms exponentially increasing in the time may appear in the solutions in addition to those given.

The method used is that of the Laplace transformation following the treatment previously given in detail.[*] The solutions for the solids with zero initial temperature and for the source problems may be regarded as rigorous since it can in all cases be verified[†] that they satisfy the differential equations and initial and boundary conditions. In deriving the solution for arbitrary initial temperature $f(r)$ from the rigorous source solution, assumptions are made and by letting $t \rightarrow 0$ in these results interesting expansion theorems are obtained, but only formally. The corres-

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[*] Carslaw and Jaeger, *Phil. Mag.*, (7). XXVI (1938), 473 ; *Proc. London Math. Soc.*, **46** (1940), 361 : *Proc. Cambridge Phil. Soc.*, XXXV (1939), 394. These papers will be referred to as I, II and III respectively.

[†] For a complete exposition of the method of doing this, see III.

ponding problems with spherical and plane boundaries may be discussed in the same way ; the solutions are much simpler since they involve trigonometrical in place of Bessel functions.

In § 2 the solid cylinder with zero initial temperature is discussed, and in § 3 the instantaneous cylindrical surface source in the solid cylinder. In § 4 the corresponding results for the hollow cylinder are given. In §§ 5 and 6 the region bounded internally by a circular cylinder is discussed. In § 7 a few typical problems which lead to boundary conditions of type (1) are collected.

2. *The solid cylinder $0 < r < a$ with zero initial temperature and boundary condition* (1) *at $r = a$.*

We have to solve

$$\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r} = \frac{1}{\varkappa}\frac{\partial r}{\partial t}, \quad 0 < r < a, \ t > 0 \quad \dots\dots\dots (2)$$

with $v = 0$, when $t = 0$, $0 < r < a$ $\dots\dots\dots\dots (3)$

and $k_1 \dfrac{\partial r}{\partial t} + k_2 \dfrac{\partial r}{\partial r} + k_3 v = k_4$, $r = a$, $t > 0$ $\dots\dots\dots (4)$

As in I, we multiply the differential equation (2) and its boundary condition (4) by e^{-pt}, $p > 0$, and integrate with respect to t from 0 to ∞. Then writing, as always,

$$\bar{v} = \int_0^\infty e^{-pt} r \, dt \quad \dots\dots \dots\dots \dots\dots \dots\dots (5)$$

for the Laplace transform of r we obtain the " subsidiary equation "

$$\frac{d^2\bar{r}}{dr^2} + \frac{1}{r}\frac{d\bar{r}}{dr} - q^2 r = 0, \quad 0 < r < a \quad \dots\dots \dots\dots (6)$$

where $q^2 = p/\varkappa$ $\dots\dots\dots \dots\dots \dots\dots\dots \dots\dots (7)$

This has to be solved with boundary condition

$$(k_1 p + k_3)\bar{r} + k_2\frac{dr}{dr} = \frac{k_4}{p}, \quad \text{when } r = a \quad \dots\dots (8)$$

The solution of (6) which satisfies (8) is

$$\bar{r} = \frac{k_4 I_0(qr)}{p\{(k_1 p + k_3) I_0(qa) + k_2 q I_1(qa)\}} \quad \dots \quad \dots\dots (9)$$

$v(t)$ is found from $\bar{r}(p)$ by the inversion theorem for the Laplace transformation, which states that, subject to certain conditions,

$$v(t) = \frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} e^{\lambda t}\bar{r}(\lambda)d\lambda \quad \dots\dots\dots\dots\dots\dots (10)$$

where γ is a positive constant such that all singularities of $\bar{v}(\lambda)$ lie to the left of $R(\lambda) = \gamma$. Using this result we find from (9)

$$v = \frac{k_4}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} \frac{e^{\lambda t} I_0(\mu r) d\lambda}{\lambda\{(k_1\lambda + k_3)I_0(\mu a) + k_2\mu I_1(\mu a)\}} \quad \dots \quad (11)$$

where $\mu = \sqrt{(\lambda/\varkappa)}$ $\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots$ (12)

The integrand of (11) is a single valued function of λ with a simple pole at $\lambda = 0$ of residue $1/k_3$ (provided* $k_3 \neq 0$). It has also poles at $\lambda = -\varkappa\alpha_s^2$, where $\pm\alpha_s$, $s = 1, 2, \dots$, are the roots (all real† and simple) of

$$(k_3 - k_1\varkappa\alpha^2)J_0(a\alpha) - k_2\alpha J_1(a\alpha) = 0 \quad \dots\dots\dots (13)$$

Also

$$\left[\lambda\frac{d}{d\lambda}\{(k_1\lambda + k_3)I_0(\mu a) + k_2\mu I_1(\mu a)\}\right]_{\lambda = -\varkappa\alpha_s^2}$$

$$= -\frac{a}{2k_2}\{k_2(k_2 + 2k_1\varkappa/a)\alpha_s^2 + (k_3 - k_1\varkappa\alpha_s^2)^2\}J_0(a\alpha_s)$$

$$\dots\dots\dots\dots\dots\dots (14)$$

and using this result the residue of the integrand of (11) at the pole $\lambda = -\varkappa\alpha_s^2$ can be written down.

To evaluate the line integral (11) we consider the closed contour of Fig. 1 consisting of portion of the line $R(\lambda) = \gamma$ and portion of a circle Γ, centre the origin and enclosing it, whose radius takes a sequence of values $\{R_n\}$ avoiding the poles of the integrand. Then as in II and III it may be shown that the integral over Γ tends to zero as $n \to \infty$ and thus the line integral in (11) equals $2\pi i$ times the sum of the residues at its poles. These have already been evaluated, and collecting them we obtain finally

$$v = \frac{k_4}{k_3} - \frac{2k_2k_4}{a}\sum_{s=1}^{\infty}\frac{e^{-\varkappa\alpha_s^2 t}J_0(r\alpha_s)}{\{k_2(k_2 + 2k_1\varkappa/a)\alpha_s^2 + (k_3 - k_1\varkappa\alpha_s^2)^2\}J_0(a\alpha_s)}$$

$$\dots\dots\dots\dots\dots\dots (15)$$

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* If $k_3 = 0$ there is a double pole at $\lambda = 0$; poles of higher order may also arise.

† If the constants k are unrestricted, the integrand of (11) may have a pole for real positive λ, i.e. (13) may have an imaginary root. Corresponding to a real positive pole of $\bar{v}(\lambda)$ there will be an additional term in the solution v exponentially increasing in the time. As stated in § 1, these cases will not be considered as being of no practical importance. If the constants k have values derived from problems of the types discussed in § 7, it may be verified as in II and III that the roots are all real and simple.
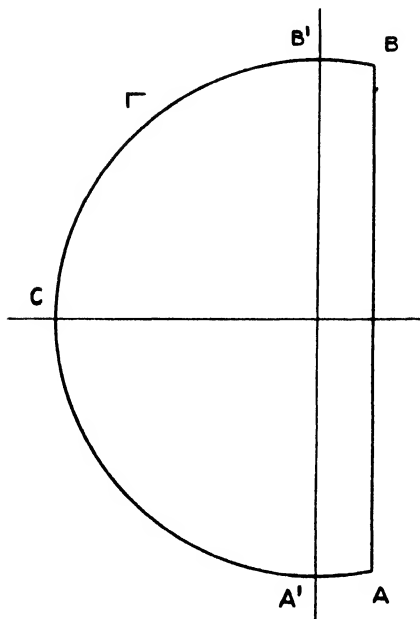
Fig. 1.

3. *The solid cylinder* $0 \leqslant r < a$. *An instantaneous cylindrical surface source* * *of strength* Q *over* $r = r'$ *at* $t = 0$. *Boundary condition*

$$k_1 \frac{\partial v}{\partial t} + k_2 \frac{\partial v}{\partial r} + k_3 v = 0, \ r = a, \ t > 0 \ \ldots \ldots \ldots \ (16)$$

We have to solve

$$\frac{\partial^2 v}{\partial r^2} + \frac{1}{r} \frac{\partial v}{\partial r} = \frac{1}{\varkappa} \frac{\partial v}{\partial t}, \ 0 \leqslant r < a, \ t > 0$$

with the boundary condition (16) and with

$$v = u + w \ \ldots \ldots \ldots \ldots \ldots \ldots \ (17)$$

where $u = \dfrac{Q}{4\pi\varkappa t} exp\left[-\dfrac{r^2 + r'^2}{4\varkappa t} \right] I_0\!\left(\dfrac{rr'}{2\varkappa t} \right) \ \ldots \ldots \ldots \ (18)$

and w satisfies

$$\frac{\partial^2 w}{\partial r^2} + \frac{1}{r} \frac{\partial w}{\partial r} = \frac{1}{\varkappa} \frac{\partial w}{\partial t}, \ 0 \leqslant r < a, \ t > 0 \ \ldots \ldots \ (19)$$

and $\displaystyle\lim_{t \to 0} \ w = 0, \ 0 \leqslant r < a \ \ldots \ldots \ldots \ldots \ldots \ldots \ (20)$

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* See Carslaw, *Conduction of Heat*, 1921, Chapter IX.

It is known that†

$$\bar{u} = \frac{Q}{2\pi\varkappa} I_0(qr')K_0(qr), \quad r > r' \Bigg\}$$
$$= \frac{Q}{2\pi\varkappa} I_0(qr)K_0(qr'), \quad r < r' \Bigg\} \quad \dots\dots\dots (21)$$

where, as always, $q = \sqrt{(p/\varkappa)}$.

From (19) and (20) we obtain the subsidiary equation for w

$$\frac{d^2\bar{w}}{dr^2} + \frac{1}{r}\frac{d\bar{w}}{dr} - q^2\bar{w} = 0, \quad 0 \leqslant r < a.$$

The solution of this, which is finite at $r = 0$, is $AI_0(qa)$, and from (16), (17) and (21) we obtain

$$A\{(k_1p + k_3)I_0(qa) + k_2qI_1(qa)\}$$
$$= -\frac{Q}{2\pi\varkappa} I_0(qr')\{(k_1p + k_3)K_0(qa) + k_2qK_1(qa)\}.$$

Thus $v = \bar{u} + \bar{w}$

$$= -\frac{Q}{2\pi\varkappa}\frac{I_0(qr)\{I_0(qr')[(k_1p+k_3)K_0(qa)-k_2qK_1(qa)]-K_0(qr')[(k_1p+k_3)I_0(qa)+k_2qI_1(qa)]\}}{(k_1p+k_3)I_0(qa)+k_2qI_1(qa)}$$

$$\dots\dots\dots\dots\dots (22)$$

when $0 \leqslant r < r'$ and when $r' < r < a$ the result is that obtained by interchanging r and r' in (22).

v is obtained from $\bar{v}$ as in § 2 by the use of the inversion theorem and the contour of Fig. 1. $\bar{v}(\lambda)$ has no pole at $\lambda = 0$ (unless $k_3 = 0$) and simple poles at $\lambda = -\varkappa\alpha_s^2$, where $\pm\alpha_s$ are the roots of (13). The residues at these poles follow from (14) and we have finally

$$v = \frac{k_2Q}{\pi a^2} \sum_{s=1}^{\infty} \frac{e^{-\varkappa\alpha_s^2 t}J_0(r\alpha_s)J_0(r'\alpha_s)}{k_2J_1^2(a\alpha_s)+(k_3+2k_1\varkappa/a)J_0^2(a\alpha_s)} \dots\dots (23)$$

where the α_s are the roots of (13). The form (23) is symmetrical in r and r' so holds for $r \gtrless r'$.

If we put $Q = 2\pi r'f(r')dr'$ in (23), integrate with respect to r' from 0 to a, and assume that $f(r')$ is such that the orders of integration and summation may be interchanged, we obtain the solution for *the cylinder* $0 \leqslant r < a$ with initial temperature $f(r)$ and boundary condition (16)

$$v = \frac{2k_2}{a^2} \sum_{s=1}^{\infty} \frac{e^{-\varkappa\alpha_s^2 t}J_0(r\alpha_s)}{k_2J_1^2(a\alpha_s)+(k_2+2k_1\varkappa/a)J_0^2(a\alpha_s)} \int_0^a r'f(r')J_0(r'\alpha_s)dr'$$

$$\dots\dots\dots\dots (24)$$

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† This result follows from Watson, *Theory of Bessel Functions*, § 13.7.

If we let $t \to 0$ in (24) we obtain formally the expansion

$$f(r) = \frac{2k_2}{a^2} \sum_{s=1}^{\infty} \frac{J_0(r\alpha_s)}{k_2 J_1^2(a\alpha_s) + (k_2 + 2k_1\kappa/a)J_0^2(a\alpha_s)}$$
$$\int_0^a r'f(r')J_0(r'\alpha_s)dr'$$
$$\dots\dots\dots\dots (25)$$

of which the Dini series is a particular case. If $k_2 = 0$, or in the special cases referred to in § 2 (footnote), an extra term is to be added corresponding to the well known first term of a Dini series.

4. In this section results for the hollow cylinder $a < r < b$ with boundary conditions of type (1) at $r = a$ and $r = b$ will be given. The proofs follow exactly the lines of those of § 2 and § 3. It is assumed that the special cases of no practical interest referred to in § 1 and the footnote of § 2 do not occur. Also that k_3 and k'_3 do not both vanish.

(i) *The hollow cylinder $a < r < b$ with zero initial temperature and with boundary conditions*

$$k_1 \frac{\partial v}{\partial t} + k_2 \frac{\partial v}{\partial r} + k_3 v = k_4, \quad r = a, \ t > 0$$

$$k'_1 \frac{\partial v}{\partial t} + k'_2 \frac{\partial v}{\partial r} + k'_3 v = k'_4, \quad r = b, \ t > 0$$

The solution is

$$v = \frac{ak_4(k'_2 - bk'_3 \log r/b) - bk'_4(k_2 - ak_3 \log r/a)}{ak_3 k'_2 - bk_2 k'_3 - ab \ k_3 k'_3 \log a/b}$$
$$- \pi \sum_{s=1}^{\infty} e^{-\kappa\alpha_s^2 t} F(\alpha_s)C_0(r;\alpha_s)\{k_4[A'_s J_0(b\alpha_s) - k'_2\alpha_s J_1(b\alpha_s)]$$
$$- k'_4[A_s J_0(a\alpha_s) - k_2\alpha_s J_1(a\alpha_s)]\}$$
$$\dots\dots\dots\dots (26)$$

where $A_s = k_3 - \kappa k_1\alpha_s^2, \quad A'_s = k'_3 - \kappa k'_1\alpha_s^2, \quad B = k_2 + 2\kappa k_1/a,$
$B' = k'_2 + 2\kappa k'_1/b$ $\dots\dots\dots\dots\dots\dots (27)$
$$C_0(r;\alpha_s) = J_0(r\alpha_s)[A_s Y_0(a\alpha_s) - k_2\alpha_s Y_1(a\alpha_s)]$$
$$- Y_0(r\alpha_s)[A_s J_0(a\alpha_s) - k_2\alpha_s J_1(a\alpha_s)]$$
$$\dots\dots\dots\dots (28)$$

$$F(\alpha_s) = \frac{A'_s J_0(b\alpha_s) - k'_2\alpha_s J_1(b\alpha_s)}{[A'_s J_0(b\alpha_s) - k'_2\alpha_s J_1(b\alpha_s)]^2(A_s^2 + k_2 B\alpha_s^2) - [A_s J_0(a\alpha_s) - k_2\alpha_s J_1(a\alpha_s)](A'^2_s + k'_2 B'\alpha_s^2)}$$
$$\dots\dots\dots\dots (29)$$

and α_s, $s=1$, 2, ... are the positive roots of

$$[(k_3-k_1\varkappa\alpha^2)J_0(a\alpha)-k_2\alpha J_1(a\alpha)]$$
$$[(k'_3-k'_1\varkappa\alpha^2)Y_0(b\alpha)-k'_2\alpha Y_1(b\alpha)]$$
$$-[(k'_3-k'_1\varkappa\alpha^2)J_0(b\alpha)-k'_2\alpha J_1(b\alpha)]$$
$$[(k_3-k_1\varkappa\alpha^2)Y_0(a\alpha)-k_2\alpha Y_1(a\alpha)]=0$$
$$\ldots\ldots\ldots\ldots\ldots (30)$$

(ii) *The hollow cylinder $a<r<b$. An instantaneous cylindrical surface source of strength Q over $r=r'$ at $t=0$. Boundary conditions*

$$k_1\frac{\partial v}{\partial t}+k_2\frac{\partial v}{\partial r}+k_3v=0, \quad r=a, \ t>0$$
$$\ldots\ldots\ldots\ldots\ldots (31)$$
$$k'_1\frac{\partial v}{\partial t}+k'_2\frac{\partial v}{\partial r}+k'_3v=0, \ r=b, \ t>0.$$

$$v=-\frac{\pi Q}{4}\sum_{s=1}^{\infty}\alpha_s^2 e^{-\varkappa\alpha_s^2 t}[A'_s J_0(b\alpha_s)-k'_2\alpha_s J_1(b\alpha_s)]$$
$$F(\alpha_s)C_0(r;\alpha_s)C_0(r';\alpha_s)$$
$$\ldots\ldots\ldots\ldots\ldots (32)$$

where the α_s are the positive roots of (30) and A'_s, $F(\alpha_s)$ and $C_0(r;\alpha_s)$ are defined in (27) (29) and (28).

If we put $Q=2\pi r'f(r')dr'$, integrate from a to b, and assume $f(r')$ is such that the orders of integration and summation can be reversed, we obtain the solution for *the cylinder with initial temperature $f(r)$ and boundary conditions* (31)

$$v=-\frac{\pi^2}{2}\sum_{s=1}^{\infty}\alpha_s^2 e^{-\varkappa\alpha_s^2 t}[A'_s J_0(b\alpha_s)-k'_2\alpha_s J_1(b\alpha_s)]F(\alpha_s)C_0(r;\alpha_s)$$
$$\int_a^b C_0(r';\alpha_s)f(r')r'dr'$$
$$\ldots\ldots\ldots\ldots\ldots (33)$$

Letting $t\to 0$ we obtain formally the expansion theorem

$$f(r)=-\frac{\pi^2}{2}\sum_{s=1}^{\infty}\alpha_s^2[A'_s J_0(b\alpha_s)-k'_2\alpha_s J_1(b\alpha_s)]F(\alpha_s)C_0(r;\alpha_s)$$
$$\int_a^b C_0(r';\alpha_s)f(r')r'dr'$$
$$\ldots\ldots\ldots\ldots\ldots (34)$$

5. *The region bounded internally by the cylinder $r=a$ with zero initial temperature and boundary condition*

$$k_1\frac{\partial v}{\partial t}+k_2\frac{\partial v}{\partial r}+k_3v=k_4, \quad r=a, \ t>0.$$

Proceeding as in § 2, the transform $\bar{v}$ is found to be

$$\bar{v} = \frac{k_4 K_0(qr)}{p\{(k_1 p + k_3)K_0(qa) - k_2 q K_1(qa)\}} \quad \ldots \ldots \ldots (35)$$

And thus, using the inversion theorem,

$$v = \frac{k_4}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} \frac{e^{\lambda t} K_0(\mu r) d\lambda}{\lambda\{(k_1 \lambda + k_3)K_0(\mu a) - k_2 \mu K_1(\mu a)\}}$$

$$\ldots \ldots \ldots \ldots \ldots (36)$$

where $\mu = \sqrt{(\lambda/\varkappa)}$.
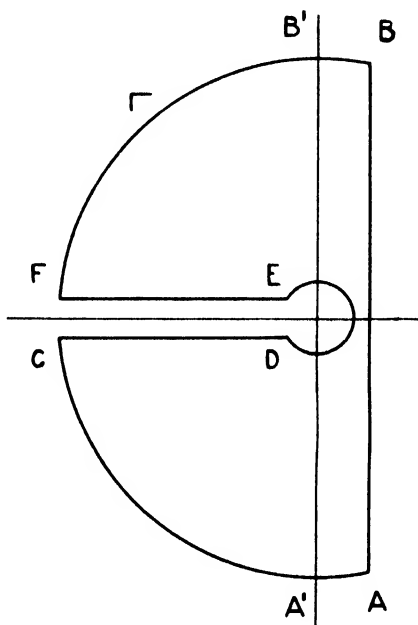
Fig. 2.

The integrand of (36) has a branch point at the origin and no other singularities. To evaluate it we consider the integral round the closed circuit of Fig. 2 consisting of the line AB distant γ from the imaginary axis, arcs BF and AC of a large circle Γ whose radius will tend to infinity, the lines CD and EF on which arg λ equals $-\pi$ and π respectively, and a small circle about the origin whose radius will tend to zero. Then, as in II and III, it follows that the integral over Γ tends to zero as the radius tends to infinity. Thus in the limit the integral in (36) may be replaced by the sum of the integrals over CD and EF and the small circle.

The small circle gives* k_4/k_3.

On CD and EF we put $\lambda = \kappa u^2 e^{-i\pi}$ and $\lambda = \kappa u^2 e^{i\pi}$ respectively and obtain

$$\frac{k_4}{2i\pi}\int_0^\infty \frac{2e^{-\kappa u^2 t}du}{u}\left\{\frac{K_0(iur)}{(k_3-k_1\kappa u^2)K_0(iua)-ik_2uK_1(iua)}\right\}$$
$$+\text{conjugate}.$$

Combining these results we have finally

$$v=\frac{k_4}{k_3}+\frac{2k_4}{\pi}\int_0^\infty \frac{e^{-\kappa u^2 t}C_0(u;r)du}{u\varphi(u)} \quad \dots\dots\dots (37)$$

where

$$C_0(u;r)=J_0(ur)[(k_3-k_1\kappa u^2)Y_0(ua)-k_2uY_1(ua)]$$
$$-Y_0(ur)[(k_3-k_1\kappa u^2)J_0(ua)-k_2uJ_1(ua)]$$
$$\dots\dots\dots\dots (38)$$

and $\varphi(u)=[(k_3-k_1\kappa u^2)J_0(ua)-k_2uJ_1(ua)]^2$
$$+[(k_3-k_1\kappa u^2)Y_0(ua)-k_2uY_1(ua)]^2$$
$$\dots\dots\dots\dots (39)$$

6. *The region bounded internally by the cylinder* $r=a$. *An instantaneous cylindrical surface source of strength* Q *over* $r=r'$. *The boundary condition*

$$k_1\frac{\partial v}{\partial t}+k_2\frac{\partial v}{\partial r}+k_3v=0, \; r=a, \; t>0 \dots\dots\dots (40)$$

Proceeding as in § 3 the transform of v is found to be

$$\bar{v}=\frac{Q}{2\pi\kappa}\frac{K_0(qr')\{I_0(qr)[(k_1p+k_3)K_0(qa)-k_2qK_1(qa)]-K_0(qr)[(k_1p+k_3)I_0(qa)+k_2qI_1(qa)]\}}{(k_1p+k_3)K_0(qa)-k_2qK_1(qa)}$$
$$\dots\dots\dots\dots (41)$$

when $a<r<r'$ and when $r>r'$ the result is obtained by interchanging r and r' in (41).

Thus, using the inversion theorem and the contour of Fig. 2, we obtain in the notation of (38) and (39)

$$v=\frac{Q}{2\pi}\int_0^\infty e^{-\kappa u^2 t}\frac{C_0(u;r)C_0(u;r')udu}{\varphi(u)} \quad \dots\dots\dots (42)$$

and this result, being symmetrical in r and r', holds for $r \gtrless r'$.

If we put $Q=2\pi r'f(r')dr'$ and integrate with respect to r' from a to ∞, assuming the orders of integration can be

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* It is assumed in this section and the next that $k_2 \neq 0$.

interchanged, we obtain the solution for the region with
initial temperature $f(r)$ and boundary conditions (40)

$$v = \int_0^\infty e^{-\varkappa u^2 t} \frac{C_0(u;r)u\,du}{\varphi(u)} \int_a^\infty f(r')C_0(u;r')r'dr' \quad \ldots (43)$$

Letting $t \to 0$ we obtain formally

$$f(r) = \int_0^\infty \frac{C_0(u;r)u\,du}{\varphi(u)} \int_a^\infty f(r')C_0(u;r')r'dr' \quad \ldots\ldots (44)$$

a generalisation of Weber's integral theorem and of the
more general integral theorem given by Goldstein [*Proc.
London Math. Soc.*, 34 (1931), p. 87 (225)].

7. It was remarked in § 1 that the boundary condition (1)
included several cases of practical importance. Most of
these arise from problems in which the cylinder is in
contact at its boundary with well stirred liquid which may
be regarded as a perfectly conducting body. Some
examples of the hollow cylinder theory of § 4 are given
below, similar applications of the theory of the other
sections suggest themselves.

(i) *The region $r < a$ is perfectly conducting; it has density
ρ' and specific heat c'. Heat is supplied to it at rate H per
unit time, per unit length, for $t > 0$. The region $a < r < b$
has conductivity K, specific heat c, and density ρ. At
$r = b$ there is radiation into a medium at zero, $\dfrac{\partial v}{\partial r} + hv = 0$.
The initial temperature of the whole is zero.*

Here the boundary condition at $r = a$ is

$$\pi a^2 \rho' c' \frac{\partial v}{\partial t} = 2\pi a K \frac{\partial v}{\partial r} + H.$$

Thus in the notation of § 4 (i)

$$k_1 = \pi a^2 \rho' c', \quad k_2 = -2\pi a K, \quad k_3 = 0, \quad k_4 = H$$
$$k'_1 = 0, \qquad k'_2 = 1, \qquad k'_3 = h, \quad k'_4 = 0.$$

This problem occurs in the theory of hot water systems,
also it is an approximation to the case of an insulated wire
heated by electric current.

(ii) *The region $r < a$ contains perfectly conducting fluid
of density ρ' and specific heat c'. The region $a < r < b$ is a
conductor K, ρ, c. At $r = b$ there is radiation into medium
at zero. The initial temperature of the whole is zero. For
$t > 0$ volume Q of fluid is removed per unit time per unit
length from the interior and replaced by fluid at V.*

The boundary condition at $r=a$ is

$$\pi a^2 \rho' c' \frac{\partial v}{\partial t} = 2\pi a K \frac{\partial v}{\partial r} + Q\rho' c'(V-v).$$

So in the notation of § 4 (i)

$$k_1 = \pi a^2 \rho' c', \quad k'_2 = -2\pi a K, \quad k_3 = Q\rho' c', \quad k_4 = Q\rho' c' V$$
$$k'_1 = 0, \qquad k'_2 = 1, \qquad k'_3 = h, \qquad k'_4 = 0.$$

(iii) *The region $r < a$ contains mass M' per unit length of perfectly conducting fluid of specific heat c' which is removed at the rate m' per unit length per unit time and replaced by fluid at V. The region $r > b$ contains mass M'' per unit length of perfectly conducting fluid of specific heat c'' which is removed at the rate m'' per unit length per unit time and replaced by fluid at zero. The region $a < r < b$ is a conductor K, ρ, c. The initial temperature of the whole is zero.*

Here in the notation of § 4 (i)

$$k_1 = M'c', \quad k_2 = -2\pi a K, \quad k_3 = m'c', \quad k_4 = m'c'V$$
$$k'_1 = M''c'', \quad k'_2 = 2\pi b K, \quad k'_3 = m''c'', \quad k'_4 = 0.$$

(iv) Problems in which the flux over a boundary is prescribed are included in the theory.

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THE DETECTION AND ESTIMATION OF α-TERPINENE BY MEANS OF THE DIENE SYNTHESIS.

By R. M. GASCOIGNE, B.Sc.

Applications of the diene synthesis in terpene chemistry have been fruitful, not only in synthesis but also in the characterisation of individual terpenes and in the separation of hydrocarbon mixtures. Thus the adduct of α-phellandrene and maleic anhydride has now superseded the nitrosite for the characterisation of this terpene (Birch, THIS JOURNAL, 1937, *71*, 261 ; Goodway and West, *J. Soc. Chem. Ind.*, 1937, *56*, 472T), and further forms the basis of methods for its estimation (Birch, THIS JOURNAL, 1937, *71*, 54 ; Hancox and Jones, *Univ. Qld. Papers in Chem.*, 1939, *1*, No. 14).

In the case of α-terpinene, the only other naturally occurring conjugated p-menthadiene (except β-phellandrene, which reacts abnormally) (cf. Goodway and West, *J.C.S.*, 1938, 2028), the diene synthesis has been investigated with two philodienes, acetylene dicarboxylic ester (Alder and Rickert, *Berichte*, 1937, *70*, 1364) and maleic anhydride (Diels, Koch and Frost, *ibid.*, 1938, *71*, 1163). In both instances the product of the dehydration of α-terpineol was used as α-terpinene. In the latter case the reaction was investigated only at the boiling point of the terpene, in contrast to α-phellandrene, which reacts readily in the cold, and it was regarded as doubtful whether the reaction proceeded normally and whether the adduct had the expected structure. This appeared to be supported by the fact that the reaction with p-benzoquinone did not proceed readily—again in contrast to α-phellandrene.

Later, however, Alder (*Berichte*, 1938, *71*, 2210) pointed out that by analogy with the acetylene dicarboxylic ester adduct the maleic anhydride adduct should be normal and that there was no definite evidence to the contrary.

In the present paper the isolation of the α-terpinene p-benzoquinone adduct is described and it is shown that

the reaction between α-terpinene and maleic anhydride proceeds quantitatively at ordinary temperature. Consequently Birch's method of estimation is applicable to this terpene. The results of the estimation show that the ordinary preparation of α-terpinene, by the dehydration of α-terpineol, gives a product containing only about 50% of α-terpinene. Similarly Birch found that many specimens of " α-phellandrene " contained only small percentages of that terpene.

In order to show that α-terpinene reacts quantitatively with maleic anhydride it was necessary to obtain a pure specimen of α-terpinene. This terpene is difficult to obtain reasonably pure ; according to Simonsen " the hydrocarbon cannot be obtained in a state of purity and is always contaminated to a greater or less degree with other terpenes " (" The Terpenes ", Vol. I, p. 147). The best method of purification appeared to be that of Richter and Wolff (Berichte, 1930, 63, 1720), who regenerated α-terpinene from its solid dihydrochloride by means of aniline and carefully fractionated the product. Terpinolene and γ-terpinene were shown to be present in the higher fractions. A specimen of α-terpinene prepared by this method was found to be 94% absorbed by maleic anhydride in the Birch estimation. Since it is very probable that the 6% unabsorbed was due to the presence of other terpenes or p-cymene, it is reasonable to conclude that the absorption of α-terpinene is quantitative.

The limitations of the estimation have been discussed by Birch. It is obviously inapplicable when more than one conjugated diene is present, unless only the " diene value " is required. It should be emphasised that while the dienes combine quantitatively with maleic anhydride, the formation of the crystalline adducts is not quantitative, due to the formation of resinous adducts. This is particularly the case when the terpenes are heated with maleic anhydride.

Kaufmann's method of determining the " diene number " of fats and oils by heating with maleic anhydride and determining the excess of the anhydride iodimetrically has been applied to α-terpinene (Berichte, 1937, 70, 903) and α-phellandrene (Hancox and Jones, loc. cit.). This method is considered unreliable by Goodway and West (J. Soc. Chem. Ind., 1938, 57, 37T) and others (cf. Chem. Abstracts, 1940, 34, 975 ; Bull. Soc. Chim., 1937 (V), 4, ii, 2105).

Although α-phellandrene reacts readily with p-benzo-quinone forming a well crystallised adduct, the only mention of α-terpinene in this respect is a reference by Alder to the " rather unsatisfactory course of the addition of the terpene to quinone " (*Berichte*, 1938, *71*, 2211). It appears that α-terpinene is partially oxidised to p-cymene by the quinone ; the great ease of oxidation of α-terpinene has been demonstrated by Richter and Wolff (*loc. cit.*). The quinone is reduced only to quinhydrone ; apparently the terpene is incapable of reducing it completely to quinol. However, adduct formation does take place as well, and it is possible to isolate a beautifully crystalline adduct in 29% yield.

The maleic anhydride and benzoquinone adducts of α-terpinene, like those of α-phellandrene, can be applied advantageously to the detection and characterisation of the terpene, especially when present in small amounts in mixtures.

EXPERIMENTAL.

Detection of α-Terpinene by the Maleic Anhydride Adduct.

This was carried out as described by Birch (*loc. cit.*) for α-phellandrene except that before the steam distillation the mixture was heated with excess 20% sodium hydroxide solution on the water bath for five minutes with continuous shaking. After the steam distillation the precipitated sodium salt was filtered off, washed well with alcohol and ether·and dissolved in the minimum amount of boiling water. Addition of 20% sulphuric acid to the cooled solution precipitated the free acid as an oil which immediately crystallised. It was filtered, washed free of acid, and converted to the anhydride by leaving in an oven at 130° for an hour. Recrystallisation from light petroleum gave extremely fine needles, which felted together to form hard lumps and melted at 60°/61°.

Estimation.

The insolubility of the sodium salt of the α-terpinene adduct makes Birch's first method inapplicable. However, the second method, involving steam distillation into a Cassia flask, can be carried out exactly as described.

α-Terpinene from Terpinene Dihydrochloride.

α-Terpinene (160 g.), regenerated from its dihydrochloride as described by Wallach (*Annalen*, 1906, *350*, 148), was found

to be absorbed to the extent of 44% by maleic anhydride. After four fractionations at 29 mm. through a 20 cm. Widmer spiral in a current of nitrogen the α-terpinene content of each of the final fractions was estimated, with the following results :

Fraction.	B.P. at 29 mm.	Weight.	Percentage by Volume Absorbed.
1	75°–76°	8·5 g.	94
2	76°–77°	15·0 g.	85
3	77°–78°	17·5 g.	73
4	78°–79°	17·5 g.	62
5	79°–81°	25·0 g.	55
6	81°–83°	46·5 g.	45

The unabsorbed oil recovered from the estimations yielded terpinolene tetrabromide, m.p. 116°, but no derivative of γ-terpinene could be obtained.

α-Terpinene from Terpineol.

Dehydration of α-terpineol by hot dilute sulphuric acid as described by Wallach (*Annalen*, 1893, *275*, 105)' gave a 52% yield of a fraction boiling at 175°-177° at 762 mm. Estimation of this product by Birch's method gave an α-terpinene content of 52%.

The reaction between this product at its boiling point and maleic anhydride has been investigated by Diels, Koch and Frost (*loc. cit.*) ; the following account gives some modifications.

The terpineol dehydration product (136 g.) was heated with maleic anhydride (100 g.) as described by Diels, Koch and Frost except that after the initial vigorous reaction the mixture was not further refluxed. The unchanged terpene and maleic anhydride were distilled off up to 130° at 20 mm. and the remainder distilled between 155° and 200° at 2 mm. The distillate was mixed with an equal volume of light petroleum, filtered from fumaric acid and left in a freezing mixture, enough ethyl acetate being added to retain miscibility. After three hours the crystallised α-terpinene maleic anhydride adduct was filtered off and a further quantity obtained from the filtrate through the

sodium salt as already described. Total yield, 52 g., 22%. After two recrystallisations from light petroleum the adduct melted at 60°/61°.

Diels, Koch and Frost state that this substance melts at 66°/67° and the corresponding acid at 158°. The melting point of the acid has been found to vary with the time of heating and specimens have been obtained with melting points ranging from 126°/128° to 140°/141°, although all were prepared from the purified sodium salt. Alder and Stein (*Annalen*, 1934, *514*, 19) mention the difficulty of obtaining such acids pure due to their great tendency to anhydride formation. The acid in question is partially transformed to the anhydride in twenty-four hours (cf. Hultzsch, *Berichte*, 1939, *72*, 1177).

The figures quoted by Diels, Koch and Frost for these two melting points have also been disputed by Goodway and West (*J.C.S.*, 1940, 702), who obtained 62° and 134° respectively.

Action of p-Benzoquinone on α-Terpinene.

94% α-terpinene (2 ml., 1 mol.) was added to quinone (1·33 g., 1 mol.) in acetone (10 ml.). An immediate red coloration resulted. The solution was refluxed for two hours, then the solvent evaporated off and the quinhydrone drained on tile. It was obtained pure after one recrystallisation from alcohol, m.p. 170°, not depressed by admixture with an authentic specimen.

94% α-terpinene (1 ml., 1 mol.) was refluxed with quinhydrone (1·34 g., 1 mol.) in acetone (20 ml.) for two hours. On evaporation of the acetone the quinhydrone was recovered unchanged.

70% α-terpinene (fraction 68°-72° at 25 mm. of terpineol dehydration product ; 11·7 g., 1 mol.) was refluxed with quinone (22·1 g., 2·5 mol.) in alcohol (80 ml.) for two hours. The mixture was steam distilled and the residue cooled in ice. On pouring off the aqueous portion there remained a dark red tar which on treatment with a little methyl alcohol readily crystallised. Yield of α-terpinene benzo-quinone adduct : 4·2 g., 29% ; recrystallised twice from methyl alcohol with charcoal ; light yellow rectangular plates, m.p. 87°/88°.

Found : C=78·4, H=8·0% ; calculated for $C_{16}H_{20}O_2$, C=78·7, H=8·2%.

ACKNOWLEDGMENTS.

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THE FISSION OF THE CYCLOPROPANE RING OF α-THUJENE.

By R. M. GASCOIGNE, B.Sc.

The outstanding feature of the structure of the terpenes of the thujane group is the presence of a cyclopropane ring. The comparative instability of this ring is responsible for the characteristic reactions of these terpenes, such as the addition of water or hydrogen chloride to form alcohols and hydrochlorides derivable from α-terpinene (I).

Examples of the fission of the cyclopropane ring in these compounds forming monocyclic terpenes are firstly the isomerisation of sabinene (II) to α-terpinene by means of dilute acid (Wallach, *Annalen,* 1906, *350,* 165), and secondly the hydrogenation of α-thujene (III) and sabinene to 1 : 2-dimethyl 3-isopropyl cyclopentane (IV) (Kasansky, *Berichte,* 1929, *62,* 2206 ; Richter, Wolff and Presting, *ibid.,* 1931, *64,* 871).

The fission of the cyclopropane ring of α-thujene by dilute acid with formation of α-terpinene takes place as readily as with sabinene. In this connection the well crystallised adducts of α-terpinene with maleic anhydride and p-benzoquinone provide a convenient means of identifying this terpene, and also of eliminating it from the reaction mixture, since it reacts quantitatively with maleic anhydride (Gascoigne, THIS JOURNAL, 1940, *74,* 355). By this means it is found that the product of the action of dilute acid on α-thujene contains, besides α-terpinene, another terpene which does not react in the cold with maleic anhydride. This terpene has been shown to be γ-terpinene (V) by the preparation of several characteristic crystalline derivatives and especially by the identity of its dihydrochloride with α-terpinene dihydrochloride (cf. Richter and Wolff, *Berichte,* 1927, *60,* 477 ; Francesconi and Sernagiotto, *Gazzetta,* 1913, *43,* i, 613).

Since γ-terpinene, like many other terpenes, is easily isomerised to α-terpinene by dilute acid, it is possible that
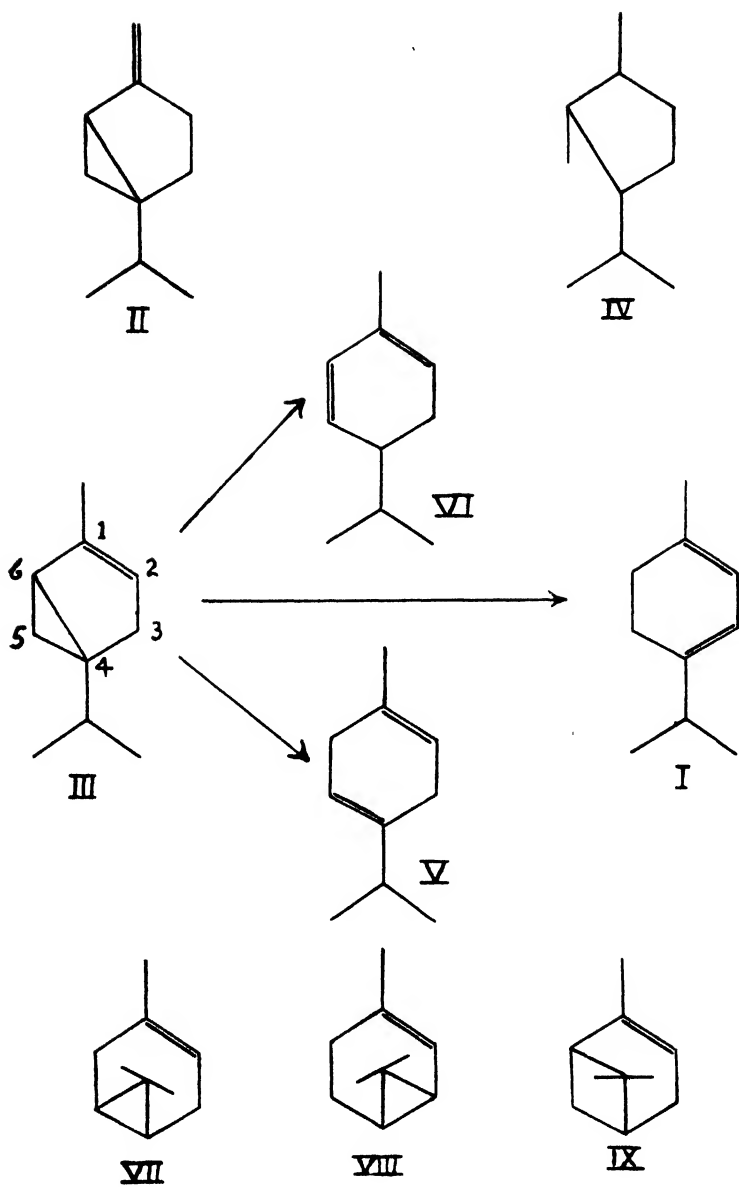
when the cyclopropane ring of α-thujene breaks, γ-terpinene is first formed and is then partially isomerised to α-terpinene.

The rupture of the C_4/C_6 bond of α-thujene might be expected to lead to the formation, besides γ-terpinene, of the alternative possibility, namely α-phellandrene (VI). This terpene is in fact formed in the reaction between α-thujene at its boiling point and maleic anhydride, and can be isolated as its maleic anhydride adduct. The main product of the reaction, besides p-cymene, is however the α-terpinene adduct. Since γ-terpinene can be shown to react at its boiling point with maleic anhydride to give the α-terpinene adduct, any γ-terpinene formed in this reaction must be immediately isomerised.

Since the α-thujene used is isolated from *E. dives* oil, in which it occurs associated with large amounts of α-phellandrene, it might seem that the appearance of α-phellandrene in the above reaction could be due to the presence of this terpene in the α-thujene. However, the α-phellandrene obtained from the ring fission of α-thujene is racemic, as is to be expected from stereochemical considerations, whilst the α-phellandrene of *E. dives* oil is lævorotatory. Moreover the α-thujene used was freed from the last traces of α-phellandrene by leaving it to stand with an excess of maleic anhydride in the cold.

The opening of the cyclopropane ring of $\triangle^3$- or $\triangle^4$-carene (VII and VIII) and the cyclobutane ring of α-pinene (IX) by maleic anhydride with the formation, in each case, of both the α-terpinene and α-phellandrene adducts (Hultzsch, *Berichte*, 1939, *72*, 1178) is analogous to the reaction with α-thujene. These are the only known examples of a "forced" diene synthesis, involving a double bond conjugated with a cyclopropane or cyclobutane ring.

Apparently α-phellandrene is not a product of the ring opening of α-thujene by dilute acid, firstly because no trace of its maleic anhydride adduct is to be found along with the α-terpinene product. Secondly, when the reaction is carried out in the presence of p-benzoquinone, only the α-terpinene adduct is formed; it is known that the α-phellandrene quinone adduct is formed more readily than the α-terpinene adduct (Gascoigne, *loc. cit.*).

Finally, it seems improbable that the action of dilute acid or maleic anhydride on α-thujene can lead to the rupture of the C_4/C_5 bond with the formation of a cyclopentadiene homologue derived from IV. Such a compound

would almost certainly either possess a conjugated system of double bonds or else be readily isomerised in the experimental conditions to a conjugated diene and so would form characteristic adducts with maleic anhydride and benzoquinone.

Experimental.

Isolation of α-Thujene.

The starting material was 13·6 Kg. of a low boiling fraction of *E. dives* oil kindly donated by W. K. Burnside Pty. Ltd. of Melbourne. This oil had α_D —23°·9 and contained, besides α-thujene, mainly 1-α-phellandrene, p-cymene, piperitone, and aliphatic aldehydes and alcohols boiling below 150°. It was fractionated at atmospheric pressure between 145° and 165° using a five-bulb Golodetz column, fractions being taken at each degree. After four fractionations the fractions 151°/152° to 154°/155° were combined (6·2 Kg. α_D 7°·7) and left with maleic anhydride (450 g.) in acetone (2 l) for an hour to remove the residual α-phellandrene (cf. Birch, This Journal, 1937, *71*, 332); from the rotation the α-phellandrene content could be calculated to be roughly 8% ; 1·25 equivalents of maleic anhydride were used). The product (5·8 Kg. α_D 15°·2) was then refluxed over sodium for five hours to free it from oxygenated impurities and finally refractionated. After two fractionations 4·5 Kg. of α-thujene were obtained having the following properties : b.p. 152°-153°/760 mm. $[\alpha]_D^{21}$ 19°·61, D_4^{21} 0·8337, n_D^{21} 1·4497. This product, as has been pointed out by Birch and Earl (This Journal, 1938, *72*, 55), is a partially racemised α-thujene, the optically pure substance having $[\alpha]_D$ approximately 37°.

Conversion of α-Thujene to α- and γ-Terpinene by Dilute Acid.

α-Thujene (50 ml., 41·7 g.) and 5% alcoholic hydrochloric acid (100 ml.) were initially immiscible, but on standing for about five minutes the mixture gradually became warm, with resulting miscibility. The mixture was refluxed for fifteen minutes, cooled, poured into water and the oil washed with water and left for an hour with maleic anhydride (40 g.) in acetone (60 ml.). After removal of the acetone the residue was heated on the water bath for fifteen minutes with 20% sodium hydroxide (150 ml.) and steam distilled. The precipitated sodium salt was

converted by the usual method to α-terpinene maleic anhydride adduct. Yield, 14 g., 20% ; m.p. 60°/61° not depressed by admixture with the authentic substance.

The oil recovered from the steam distillation (32 ml.) on fractionation at 24 mm. gave two fractions : (a) 80°-82°, (b) 100°-115°. (b) contained chlorine, and was probably a mixture of α-terpinene mono- and dihydrochlorides ; it was not further examined. (a) was γ-terpinene. Yield, 18·5 g., 45%.

Nitrosochloride : m.p. 109° from light petroleum.

Nitrolpiperide : m.p. 146° from ethyl acetate.

Nitrosate : m.p. 112° from light petroleum.

(Cf. Richter and Wolff, *Berichte*, 1930, *63*, 1714 ; Murayama, *Chem. Abstracts*, 1922, *16*, 1568.)

Dihydrochloride, m.p. 51° from methyl alcohol, mixed melting point with α-terpinene dihydrochloride 51°.

Addition of Maleic Anhydride to α-Thujene.

α-Thujene (136 g.) was heated with maleic anhydride (100 g.) as described for α-terpinene (Gascoigne, *loc. cit.*) ; the reaction was considerably more vigorous. The p-cymene and unchanged maleic anhydride were distilled off up to 130° at 20 mm. and the remainder distilled up to 200° at 2 mm. The viscous oil so obtained was mixed with a little light petroleum, filtered from fumaric acid, and redistilled at 2 mm., b.p. 150°-173°.

The distillate was mixed with an equal volume of light petroleum and left in a freezing mixture. After three hours the crystallised dl-α-phellandrene maleic anhydride adduct was filtered off. Yield, 7·6 g., 3% ; plates from aqueous alcohol, m.p. 91° not depressed by admixture with the authentic substance prepared by recrystallising together equal weights of the dextro and laevo adducts from bitter fennel and *E. dives* oil respectively.

The filtrate from the α-phellandrene adduct could not be further crystallised and was converted through the insoluble sodium salt to α-terpinene maleic anhydride adduct. Yield, 38 g., 16% ; fine needles from light petroleum. m.p. 60°/61°.

Formation of p-Cymene.

α-Thujene (27 g.) was heated with maleic anhydride (20 g.) as described and the mixture then steam distilled, yielding a light yellow oil (11 g., 41%), b.p. 173°-178°. This would not react with maleic anhydride, and would

not give a solid nitrosochloride, nitrosite or hydrochloride. It was not oxidised by cold aqueous chromic acid, but on boiling for three hours terephthalic acid was precipitated ; dimethyl ester, plates from methyl alcohol, m.p. 140°, not depressed by admixture with the authentic substance.

Addition of Maleic Anhydride to γ-Terpinene at its Boiling Point.

γ-Terpinene (5·5 g.) was heated with maleic anhydride (4 g.) in the usual way. Yield of α-terpinene adduct, 0·82 g., 9%. M.p. 60°/61° not depressed by admixture with the authentic substance.

Conversion of α-Thujene to α-Terpinene p-Benzoquinone Adduct.

α-Thujene (14 ml., 1 mol.) was added to a suspension of quinone (18·5 g.. 2 mol.) in 0·05 N. alcoholic hydrochloric acid (60 ml.). On warming, a deep red colour appeared, due to the formation of quinhydrone. The mixture was refluxed for two hours and then steam distilled. The α-terpinene quinone adduct was recovered from the residue as already described (Gascoigne, *loc. cit.*). Yield, 1·5 g., 7% ; recrystallised twice from methyl alcohol with charcoal m.p. 87°/88°, not depressed by admixture with the authentic adduct prepared from α-terpinene.

The quinone adduct of dl-α-phellandrene, prepared by recrystalling together equal weights of the dextro- and lævo adducts (cf. Diels and Alder, *Berichte*, 1929, *62*, 2365), melts at 91°, mixed melting point with the above product from α-thujene, 61°/65°.

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A DIRECT SYNTHESIS OF 1 : 2 : 4 : 5-TETRA-SUBSTITUTED IMINAZOLES.

By FRANCIS LIONS, B.Sc., Ph.D.,
and ERNEST RITCHIE, M.Sc.

Radziszewski (*Berichte*, 1882, *15*, 2706 ; 1883, *16*, 487, 747) described a general method of synthesis of iminazoles which consists in the interaction of a 1 : 2-dicarbonyl compound, ammonia in aqueous or alcoholic solution, and an aldehyde according to the scheme (A) :

$$
\begin{array}{c}
R-C=O \\
| \\
R'-C=O
\end{array}
+ \; NH_3 \; + \; CHO-R'' \longrightarrow
\begin{array}{c}
R-C=N \\
\| \quad\quad C-R'' \\
R-C-NH
\end{array}
$$
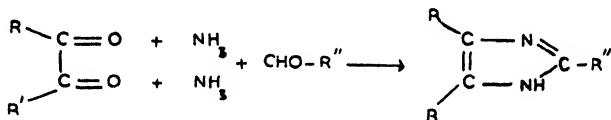
This method has been applied by numerous other workers to the synthesis of iminazoles (cf. e.g. Radziszewski and Szul, *Berichte*, 1884, *17*, 1291 ; Karcz, *Monatshefte*, 1887, *8*, 218 ; Rieger, *ibid.*, 1888, *9*, 603).

The 2 : 4 : 5-trisubstituted iminazoles available by Radziszewski's method were shown by the same author to be capable of further alkylation by an alkylhalide to the corresponding 1-alkyl-2 : 4 : 5-trisubstituted iminazole, thus :

$$
\begin{array}{c}
R-C=N \\
\| \quad\quad C-R'' \\
R'-C-NH
\end{array}
+ \; R'''-X \longrightarrow
\begin{array}{c}
R-C=N \\
\| \quad\quad C-R'', \; HX \\
R'-C-N \\
\quad\quad | \\
\quad\quad R'''
\end{array}
$$
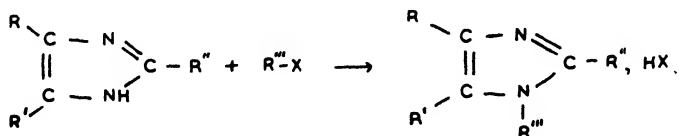
(cf. Radziszewski, *Anz. Akad. Wiss. Krakau*, 1909, 213). The method, of course, is not available for the preparation of 1-aryl-2 : 4 : 5-trisubstituted iminazoles.

A direct synthesis of 1 : 2 : 4 : 5-tetrasubstituted iminazoles carrying an aryl group attached to the 1-nitrogen atom was described by Everest and McCombie (*J.C.S.*,

1911, *99*, 1746), who reacted ammonia with acyl derivatives of α-keto-β-anilino-αβ-diphenylethane, thus :

$$
\begin{array}{ccc}
Ph-C-CH-Ph & Ph-C-CH-Ph & Ph-C=C-Ph \\
\| \quad | & \| \quad | & | \quad | \\
O \quad NH-Ph & O \quad N-Ph & N \quad N-Ph \\
& O=C & C \\
& | & | \\
& Ph & Ph
\end{array}
$$
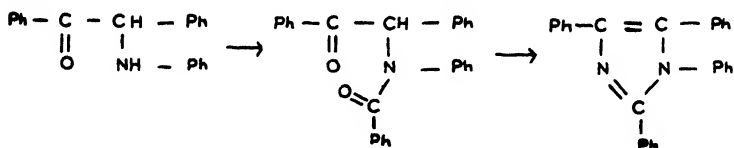
The work described in the present paper shows how it is possible to extend Radziszewski's synthesis of 2 : 4 : 5-trisubstituted iminazoles to the preparation of 1 : 2 : 4 : 5-tetrasubstituted iminazoles carrying either an alykl or an aryl group attached to the 1-nitrogen atom, by replacing one of the ammonia molecules by a molecule of a primary amine, and at the same time ensuring that the ammonia supplied shall be utilised in the reaction leading to the tetrasubstituted iminazole base, rather than a 2 : 4 : 5-trisubstituted iminazole according to the above scheme A. The most suitable method of attaining this result was to effect preliminary condensation of the 1 : 2-diketone with the primary amine in alcoholic solution at room temperature to the corresponding Schiff's base :

$$
\begin{array}{c}
R \diagdown C=O \\
| \\
R \diagup C=O
\end{array}
+ R'.NH_2 \longrightarrow
\begin{array}{c}
R \diagdown C=O \\
| \\
R \diagup C=N-R'
\end{array}
\quad I
$$
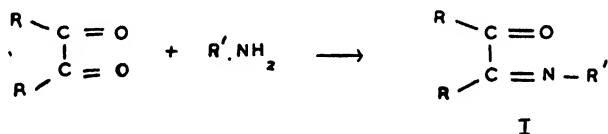
and to combine the aldehyde with ammonia to form the corresponding aldehyde-ammonia

$$
R''.CHO + NH_3 \longrightarrow R''.C\underset{NH_2}{\overset{H}{\diagup}}OH \quad II
$$
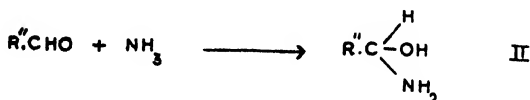
and then to allow these intermediate products I and II to react together in alcoholic solution at room temperature overnight. The resultant bases could eventually be isolated by a process of fractional distillation.

$$
\begin{array}{c}
R-C=O \\
| \\
R-C=N \\
\quad | \\
\quad R'
\end{array}
+
\begin{array}{c}
NH_2 \\
| \\
H-C-R'' \\
| \\
HO
\end{array}
\longrightarrow
\begin{array}{c}
R-C-N \\
\| \quad \diagdown C-R'' \\
R-C-N \diagup \\
\quad | \\
\quad R'
\end{array}
$$
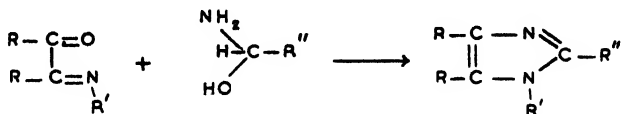
Experiments seemed to indicate that the reaction is of fairly general application. Thus, diacetyl and cyclohexan-1 : 2-dione were successfully used as α-diketones; acetaldehyde-ammonia and n-butyraldehyde-ammonia were used as intermediate II ; and methylamine, n-butylamine, benzylamine, β-phenylethylamine, aniline and p-toluidine were used as primary amines. Attempts to employ benzil as a 1 : 2-diketone were not successful.

The iminazole bases obtained were usually low melting solids or high boiling viscous oils, but they could be readily characterised as their beautifully-crystalline, sharp-melting picrates.

Attempts were also made to vary the method of synthesis by reacting one molecule to the α-diketone with one molecule of ammonia and then adding one molecule of a Schiff's base previously prepared from the aldehyde and primary amine to be employed in the synthesis, thus :

$$
\begin{array}{l}
R-C=O \\
\ \ |\\
R-C=O
\end{array}
+ NH_3
\longrightarrow
\begin{array}{l}
R-C=NH \\
\ \ | \\
R-C=O
\end{array}
+ \ \ N\overset{CH-R''}{\underset{R'}{\diagup}}
$$

$$
\begin{array}{l}
R \diagdown \\
\ \ \ C-N \diagdown \\
\ \ \| \quad\quad C-R'' \\
\ \ \ C-N\diagup \\
R \diagup \ \ |\ \\
\quad\quad R'
\end{array}
$$
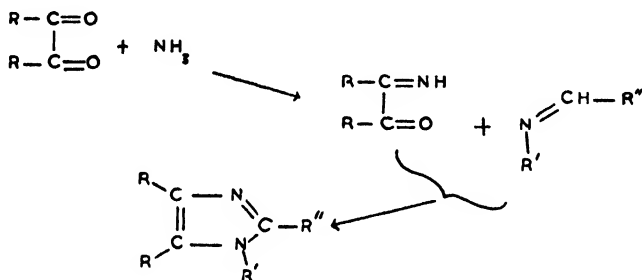
It was thought that success in this variation of the process might eventually make it possible to utilise cyclic Schiff's bases—such as 3 : 4 : 5 : 6-tetrahydropyridine (III), 3 : 4-dihydro isoquinoline, etc., and in this way to prepare condensed ring iminazole derivatives of the type (IV).

$$
\begin{array}{l}
R-C=O \\
\ \ | \\
R-C=O
\end{array}
+ NH_3
\longrightarrow
$$

III   IV
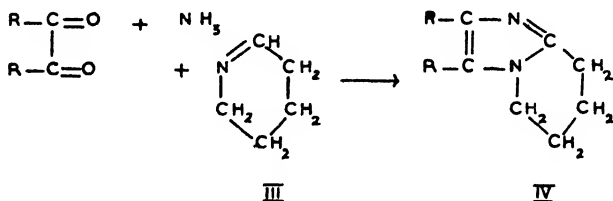
Immediate addition of ethylidene-benzylamine in alcoholic solution to a solution of diacetyl to which the correct amount of ammonia had just been added, and

allowing the mixture to stand overnight, led to formation of the expected 1-benzyl-2 : 4 : 5-trimethyliminazole, but the yield was very much less than by the method utilising the aldehyde ammonia. When diacetyl, ammonia and ethylidene-aniline were reacted together, none of the expected 1-phenyl-2 : 4 : 5-trimethyliminazole was obtained ; but some diacetyl dianil (cf. v. Pechmann, *Berichte*, 1888, *21*, 1415) was isolated, together with a small amount of a yellow picrate of a base melting at 159° which was not further examined, and much high boiling material. Finally, an application of Radziszewski's synthesis of 2 : 4 : 5-trisubstituted iminazoles is recorded, using 1 : 2-cyclohexan-dione. When treated with acetaldehyde and ammonia this diketone reacted normally, and the expected 2-methyl-4 : 5 : 6 : 7-tetrahydrobenziminazole (V) was obtained.
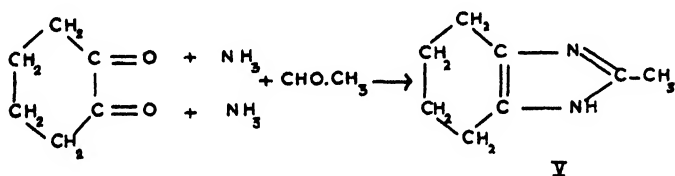
It is worthy of comment that this particular base has been previously prepared in two ways : by Hartmann and Panizzon (*Helv. Chim. Acta*, 1938, *21*, 1692) by catalytic reduction of 2-methyl benziminazole using a platinum catalyst ; and by Weidenhagen and Wegner (*Berichte*, 1938, *71*, 2124) by the action of acetaldehyde and ammonia on cyclohexanolone in presence of a cupric salt.

EXPERIMENTAL.

1 : 2 : 4 : 5-Tetramethyliminazole.

A solution of methylamine (3·1 g. ; 0·1 mol) in alcohol (20 ml.) was added during ten minutes and with constant stirring to a solution of diacetyl (8·6 g. ; 0·1 mol) in alcohol (25 ml.) at room temperature. When the reaction mixture had acquired a reddish-brown colour (10 minutes), a solution of acetaldehyde ammonia (6·1 g. ; 0·1 mol) in alcohol (40 ml.) was added. After standing overnight, sodium hydroxide solution in excess was added, and the mixture steam distilled into dilute hydrochloric acid. The distillate was concentrated to small bulk, made alkaline and the liberated bases, taken up and dried in

ether.   After removal of the solvent the residue was fractionated *in vacuo*, a pale yellow oil (2 g.) boiling at 125-8°/29 mm. which solidified almost immediately being collected.   Recrystallised from petroleum ether (60°-80°), it was obtained in colourless, diamond-shaped plates melting at 58°.

Found : $C = 67 \cdot 4$, $H = 9 \cdot 8\%$; calculated for $C_7H_{12}N_2$, $C = 67 \cdot 7$, $H = 9 \cdot 7\%$.

The base is readily soluble in water, the solution being alkaline to litmus.   Its *picrate* separates from alcohol in deep yellow rods which melt at 189°.

Found : $N = 19 \cdot 6\%$; calculated for $C_{13}H_{15}O_7N_5$, $N = 19 \cdot 8\%$.

The method above described for the synthesis of 1 : 2 : 4 : 5-tetramethyl iminazole was used for the synthesis of the bases described below, with the variation that the bases were isolated by direct fractional distillation, finally *in vacuo*, of the crude reaction mixtures which had been allowed to stand overnight.   In each instance 1/10th molecular quantities of reactants were used, and the yields stated are for pure products obtained from these quantities. The time of preliminary interaction of α-diketone with primary amine was usually adjudged to be complete when a reddish-brown colour began to appear.

1-n-Butyl-2 : 4 : 5-Trimethyliminazole.

Diacetyl (1/10th mol) and n-butylamine (1/10th mol) were reacted together in alcoholic solution at room temperature for 1 hour, and then acetaldehyde ammonia (1/10th mol) added.   A pale yellow oil (6 g. ;   36%) boiling at 145-6°/28 mm. was obtained.

Found : $C = 71 \cdot 8$, $H = 10 \cdot 6\%$; calculated for $C_{10}H_{18}N_2$, $C = 72 \cdot 3$, $H = 10 \cdot 8\%$.

This base was moderately soluble in water, giving a solution which reacted alkaline to litmus.   Its *picrate* separates from alcohol in glistening lemon-yellow flat needles melting at 145°.

Found : $N = 17 \cdot 7\%$; calculated for $C_{16}H_{21}O_7N_5$, $N = 17 \cdot 7\%$.

1-Phenyl-2 : 4 : 5-Trimethyl iminazole.

Diacetyl and aniline were reacted together in alcohol for 3 hours, then acetaldehyde ammonia added.   A pale yellow oil (6·5 g. ;   35%) boiling at 170-174°/29 mm. was collected.

Found : $C=77\cdot1$, $H=7\cdot6\%$; calculated for $C_{12}H_{14}N_2$, $C=77\cdot4$, $H=7\cdot5\%$.

The *picrate* of this base crystallises from alcohol in small yellow needles melting at 122°.

Found : $N=16\cdot8\%$; calculated for $C_{18}H_{17}O_7N_5$, $N=16\cdot9\%$.

1-p-Tolyl-2 : 4 : 5-Trimethyliminazole.

Diacetyl and p-toluidine were reacted together in alcohol for $3\frac{1}{2}$ hours and then acetaldehyde ammonia was added. A pale yellow oil (6 g. ; 30%), boiling at 176-180°/20 mm., was collected.

Found : $C=77\cdot2$, $H=8\cdot0\%$; calculated for $C_{13}H_{16}N_2$, $C=78\cdot0$, $H=8\cdot0\%$.

The *picrate* separates from alcohol in bundles of yellow needles melting at 123°.

Found : $N=16\cdot5\%$; calculated for $C_{19}H_{19}O_7N_5$, $N=16\cdot3\%$.

1-(β-Phenyl ethyl)-2 : 4 : 5-trimethyliminazole.

Diacetyl and β-phenylethylamine were allowed to react together in alcohol solution for 45 minutes and then acetaldehyde ammonia was added. A pale yellow oil (7·5 g. ; 35%) boiling at 209-212°/28 mm. was collected.

Found : $C=78\cdot3$, $H=8\cdot4\%$; calculated for $C_{14}H_{18}N_2$, $C=78\cdot5$, $H=8\cdot4\%$.

The *picrate* crystallises from ethyl alcohol in yellowish: green leaflets melting at 164°.

Found : $N=15\cdot6\%$; calculated for $C_{20}H_{21}O_7N_5$, $N=15\cdot8\%$.

1-Benzyl-2 : 4 : 5-trimethyliminazole.

(I) Diacetyl and benzylamine were reacted together in alcohol at room temperature for 30 minutes, and then acetaldehyde ammonia added. A thick pale yellow oil (7 g. ; 35%) boiling at 190-194°/26 mm. was collected. It soon solidified, and after recrystallisation from petroleum ether (40-60°) was obtained in colourless rods melting at 81°.

Found : $C=78\cdot2$, $H=8\cdot1\%$; calculated for $C_{13}H_{16}N_2$, $C=78\cdot0$, $H=8\cdot0\%$.

The *picrate* crystallises from alcohol in golden diamond-shaped plates which melt at 127°.

Found : $N=16\cdot2\%$; calculated for $C_{19}H_{19}O_7N_5$, $N=16\cdot3\%$.

(II) Alcoholic ammonia (27·2 ml., containing 1·5 g. NH_3) was added to a solution of diacetyl (8·6 g.) in alcohol (25 c.c.) and then, without delay, a solution of the Schiff's base from benzylamine (10·7 g.) and acetaldehyde (4·4 g.) in alcohol (50 c.c.) stirred in. After standing overnight the alcohol was distilled off and the residue fractionated several times *in vacuo*, the oily yellow 1-benzyl-2 : 4 : 5-trimethyliminazole (4 g. ; 13%) being eventually separated and identified as its characteristic picrate.

1 - Benzyl - 2 - methyl - 4 : 5 - cyclotetramethylene iminazole (1-Benzyl-2-methyl-4 : 5 : 6 : 7-tetrahydro benziminazole).

1 : 2-Cyclohexandione was prepared by the method of Riley, Morley and Friend (*J.C.S.*, 1932, 1878). After being allowed to stand at room temperature for some weeks it solidified spontaneously to a solid melting at 36-37°. Wallach (*Annalen*, 1924, *437*, 174) has recorded the melting point as 39-40°.

Cyclohexandione and benzylamine were reacted together in alcohol for 5 minutes and then acetaldehyde-ammonia added. A pale yellow oil (8·5 g. ; 38%) boiling at 220-4°/24 mm., which solidified on cooling, was obtained. It was recrystallised from a petroleum ether-ether mixture and thus obtained in long colourless needles melting at 76°.

Found : C=79·5, H=8·0% ; calculated for $C_{15}H_{18}N_2$, C=79·6, H=7·9%.

The *picrate* separates from alcohol in irregular lemon-yellow plates melting at 143°.

Found : N=15·4 ; calculated for $C_{21}H_{21}O_7N_5$, N=15·4%.

2-Methyl-4 : 5-cyclo-tetramethylene iminazole (2-Methyl-4 : 5 : 6 : 7-tetrahydrobenziminazole) (V).

A solution of cyclohexan-1 : 2-dione (11·2 g.) and acetaldehyde (4·4 g.) in alcohol (50 ml.) was saturated at 0° with ammonia and allowed to stand overnight at 0°. After removal of the solvent by evaporation the residue was heated to 200° *in vacuo* to remove liquid by-products, and then, after cooling, this crude product (8 g.) was recrystallised from acetone, from which it separated in small colourless needles melting at 220°.

Found : N=20·3% ; calculated for $C_8H_{12}N_2$, N=20·6%.

The *picrate* separated from alcohol in orange needles which melt at 184°.

Found : N=19·0% ; calculated for $C_{14}H_{15}O_7N_5$, N= 19·2%.

Hartmann and Panizzon (*Helv. Chim. Acta*, 1938, *21*, 1692), record the melting point of the base as 224° ; whilst Weidenhagen and Wegner (*Berichte*, 1938, *71*, 2124), record the base as melting at 221-222° and its picrate as melting at 185-6°.

n-Butyraldehyde-ammonia.

n-Butyraldehyde-ammonia was prepared by the method of Lipp (*Annalen*, 1882, *211*, 357) as follows : n-Butyraldehyde was added to excess aqueous ammonia (D. 0·96) at −10°. A curdy white precipitate formed immediately, but after 24 hours at 0° this had disappeared, leaving an oil. After a further 24 hours at 0° a copious white precipitate had formed. This was collected, washed with cold water, dried on a porous tile, and used without delay.

1-Benzyl-2-n-propyl-4 : 5-dimethyliminazole.

Diacetyl and benzylamine were reacted together in alcoholic solution for 30 minutes and then butyraldehyde ammonia added. A pale yellow oil (5·5 g. ; 24%) boiling at 194-6°/19 mm. was collected.

Found : C=78·8, H=8·3% ; calculated for $C_{15}H_{20}N_2$, C=78·9, H=8·5%.

A crystalline picrate was not isolated from this base.

Department of Chemistry,
Department of Organic Chemistry,
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THE ACTION OF HYDROGEN AND RANEY-NICKEL ON SOME AROMATIC ALDEHYDES.

By ADRIEN ALBERT, B.Sc., Ph.D.,
and BRUCE RITCHIE, B.Sc.

(With Plate XVI and one text-figure.)

In a previous paper[1] the authors showed that 2 : 4-dinitrobenzaldehyde is reduced to 2 : 4-diaminotoluene by hydrogen in two hours at atmospheric temperature and pressure in the presence of Raney-nickel. It has now been confirmed that benzaldehyde itself is not reduced under these conditions, although at a higher temperature (70° C.) it is quantitatively reduced to benzyl alcohol, no toluene being formed. Since the readier reduction of dinitrobenzaldehyde must be due to the substituent groups, it is interesting to know whether this effect is due to the nitro groups or to the amino groups formed from them by reduction.

The case in point is not one that can readily be decided from theoretical considerations. It is unsafe to assume that electronic structure plays a dominant part in catalytic reduction. If it does, the two factors involved (originally termed general polarity[2] and induced alternate polarity[3]) are here of opposite sign, and it is difficult to say how they should be equated. It is, however, a matter of general experience and has recently been shown polarographically[4] that nitro groups favour, and amino groups hinder, reduction in a molecule.

To put the matter to the test, it was decided to interrupt the reduction of 2 : 4-dinitrobenzaldehyde at different stages with a view to determining the course of the reaction. Actually the first isolated product, no matter how little hydrogen was absorbed, was a cream-coloured solid of m.pt. 165° C., insoluble in acids and alkalis and giving no reactions for aldehydes or amines. This substance was identified with a compound prepared in 1907 by Brand[5] : 2 : 2'-dinitro-4 : 4'-azoxytoluene. On further hydrogenation

A8—November 6, 1940.

it took up sufficient hydrogen to form 2 : 4-diaminotoluene and this was then isolated from the reaction mixture.

When 2 : 4-dinitrobenzaldehyde was allowed to react with rather more hydrogen (viz. 12 H, complete reduction requiring 16 H), the only different substance isolated was 2-nitro-4-aminotoluene. The course of the reaction may now be written as follows, the azoxy compound probably being formed from the union of the corresponding nitroso and hydroxylamino compounds :
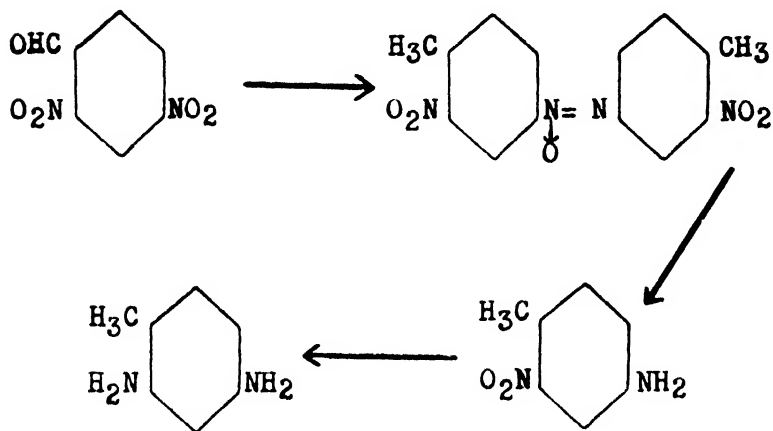
The conclusion reached is that reduction of the —CHO to —CH$_3$ takes place before any amino group is formed, and so is dependent on the molecular structure at the nitro or nitroso stage.

The reduction of 4-nitro-, 2-nitro- and 2-aminobenzaldehydes ceased, in the cold, at the benzyl alcohol stage, so that these compounds seem to be activated for reduction more strongly than benzaldehyde, and less strongly than 2 : 4-dinitrobenzaldehyde. No intermediates in these reductions could be identified, but indefinite polymeric substances were frequently obtained. The 4-nitrobenzaldehyde, reduced at a higher temperature (70° C.), gave a small amount of p-toluidine (see table) but the other substances gave rise to no o-toluidine under these conditions. On the whole, the results of reducing these mono-substituted compounds shed no light on the main problem. In a recent paper[6] it is mentioned that 3-amino-4-hydroxy-5-methoxybenzaldehyde is unchanged by hydrogenation in the presence of Raney-nickel.

Summary of Results. Reductions by Hydrogen and Raney-nickel in Alcohol, at Atmospheric Pressure.

Substance Reduced.	Amount Taken (g.)	Time. (Hours.)	Temp. °C.	Hydrogen Absorbed. (Atoms.)	Yield.	Product.	M.pt. °C.	M.pt. from Literature. °C.
Benzaldehyde	1·0	7	25	0	0		—	—
Do.	1·0	7	70	2·0	100%	Benzyl alcohol	—	—
2-Nitrobenzaldehyde	1·0	7	25	8·3	1·0 g. (65%)	2-Aminobenzyl alcohol	81	82
2-Aminobenzaldehyde	1·0	7	25	1·7	0·82 g.	Do.	81	82
4-Nitrobenzaldehyde	1·0	7	25	8·2	0·73 g.	4-Aminobenzyl alcohol	65	65
Do.	1·0	11	70	8·5 {	0·2 g. / 0·4 g.	p-Toluidine / Poly-4-aminobenzyl alcohol	40 / 212-4	43 / 214-6
2 : 4 - Dinitrobenzaldehyde	2·0	2*	25	6·0	1·4 g.	2 : 2' - Dinitro - 4 : 4' - azoxytoluene	165	164
Do.	4·0	6*	25	12·0	2·0 g.	2 - Nitro - 4 - amino- toluene	80	81
2 : 2' - Dinitro - 4 : 4' - azoxytoluene	0·2	8	50	19·6	0·14 g.	2 : 4-Diaminotoluene	98	99

* Large grains of catalyst chosen to obtain controlled reduction.

The direct hydrogenation of 2-nitrobenzaldehyde provides a useful method of preparing 2-aminobenzyl alcohol.

EXPERIMENTAL.

Procedure.—The method and catalyst used were essentially similar to those previously described[1]. The apparatus was modified (see Pl. XVI) in order to make the results more strictly quantitative, the container being an all-glass hydrogenation flask and the hydrogen being confined over mercury at atmospheric pressure. Rubber connections were kept as short as possible, and heating, when required, was supplied by a jet of steam. This form of reduction-apparatus has been found suitable as an analytical instrument for the quantitative determination of nitro- and other reducible groups.

The results obtained are summarised in the accompanying table.

2 : 2′-Dinitro-4 : 4′-azoxytoluene.—This was purified by recrystallisation from alcohol, benzene and light petroleum. M.pt. 165° C.

Found : $0 \cdot 2$ g. required for complete hydrogenation, 152 ml. hydrogen at n.t.p. ; $C_{14}H_{12}O_5N_4$ requires 138 ml.

Found : $C = 53 \cdot 3\%$, $H = 3 \cdot 9\%$. $C_{14}H_{12}O_5N_4$ requires $C = 53 \cdot 2\%$, $H = 3 \cdot 8\%$.

The other substances obtained in these reductions were characterised by the method of mixed melting points with authentic specimens.

ACKNOWLEDGMENTS.

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[1] Albert and Ritchie : THIS JOURNAL, 1940, *74*, 77.

[2] Lapworth : *Mem. Manchester Phil. Soc.*, 1920, *64*, 13.

[3] Lapworth : *Ibid.*, p. 2.

[4] Breyer : *Biochem. Zeits.*, 1939, *301*, 65.

[5] Brand : *Ber. dtsch. chem. Ges.*, 1907, *40*, 3329.

[6] Whitmore and Revukas : *J. Amer. Chem. Soc.*, 1940, *62*, 1688.
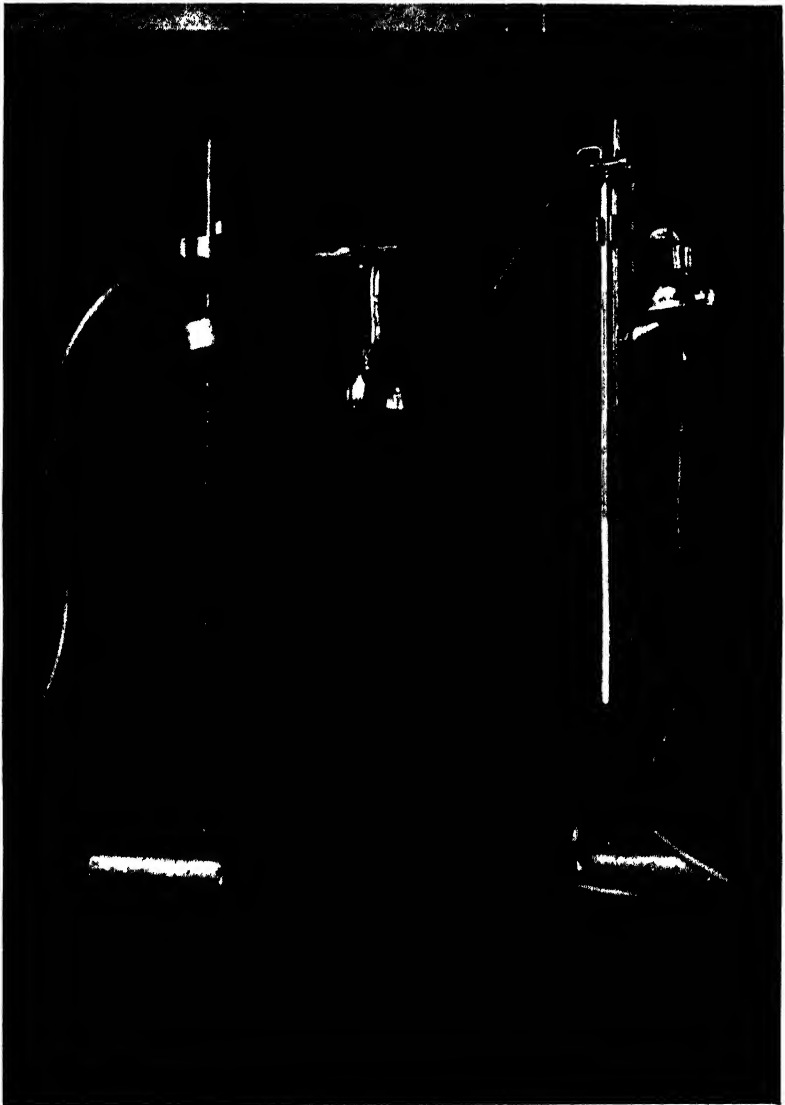
AUSTRALIAN TRIASSIC FISHES.

I. The Triassic Fishes of St. Peter's, Sydney, New South Wales.

II. The Relationships of the Australian Triassic Fishes to Each Other and to Other Bony Fishes.

By R. T. Wade, M.A., Ph.D.

I. THE TRIASSIC FISHES OF ST. PETER'S.

INTRODUCTION.

The description of the fish remains collected by Mr. B. Dunstan from five brick-pits at St. Peter's was published in 1908 (Smith Woodward, 1908).

Nearly all this original collection is in the British Museum, where, through the kindness of Dr. E. I. White, the writer was able to examine it. In the Dunstan collection the specimens of bony fishes of higher organisation than the Palæoniscidæ are few in number and poorly preserved. Since 1908, however, a small collection of nearly complete fishes from the same area has been accumulating at the Australian Museum, Sydney, where, fortunately, the type of "*Semionotus formosus*" is housed. Dr. C. Anderson, Director of the Australian Museum, very kindly placed this collection at my disposal and facilitated its examination. Hence this paper, which is intended to supplement Smith Woodward's classic memoir on this fauna.

The photograph is the work of Mr. G. C. Clutton, Australian Museum. The restoration of *Promecosomina formosa* was made by Mr. G. P. Whitley, Australian Museum.

THE ORDER OF THE UPPER STRATA IN THE SYDNEY BASIN.

In Smith Woodward's memoir the fossils are divided into those preserved in a " dark indurated shale ", thought

by the author of the memoir to be of Permian age, and those found in a " grey mudstone " which he regarded as Triassic. A note by the late W. S. Dun which accompanies the description of the fishes (in Smith Woodward, 1908, p. 30) states that both types of material were collected from the same pits and are interbedded in the same deposits ; this note seems to have been overlooked by some. For the information, therefore, of such as have not a first-hand knowledge of the geology of the Sydney basin, one may be allowed to point out that the succession of the upper strata in that area is shown quite unmistakably in very numerous deep natural sections and in bores, and by a coal mine which reaches the Permian coal measures at a depth of nearly 3,000 feet. It is known, therefore, beyond question that the Permian strata have superimposed upon them about 2,000 feet of Narrabeen shales and sand-stones, in the uppermost beds of which fishes were found at Gosford (Smith Woodward, 1890 ; Wade, 1939) ; that on these there rest about 1,000 feet of Hawkesbury sandstones, with lenticular shale beds, in one of which at about 550 feet above the Gosford horizon, the Brookvale fishes occur (Wade, 1935) ; that, finally, capping these in the area in question, come the Wianamatta shales, with the St. Peter's fish beds, which, therefore, are separated from the Permian by at least 2,000 feet of sediments.

THE AGE OF THE ST. PETER'S HORIZON.

The list of species so far obtained from the St. Peter's area is as follows :

Ichthyotomi	..	*Pleuracanthus parvidens.*
Dipnoi	..	*Ceratodus laticeps.*
Palæoniscidæ	..	*Palæoniscus antipodeus*, P. (?) *crassus, Elonichthys* (?) *armatus*, E. (?) *semilineatus, Myriolepis pectinata; Elphisopholis dunstani.*
Cleithrolepidæ	..	*Cleithrolepis granulata.*
Promecosominidæ		*Promecosomina formosa.*

Of these *Promecosomina* provides far the greatest number of individuals, *Myriolepis* the next greatest ; two specimens of *Cleithrolepis* have been recorded.

The salient features of the assemblage are as follows :

(a) The persistence of *Myriolepis* and *Cleithrolepis* throughout the whole series from the Gosford horizon upwards.

(*b*) The persistence from the Brookvale horizon of *Promecosomina* and its greatly increased importance : in the large collection from Brookvale only about five small individuals occur, but in the small Australian Museum collection of St. Peter's fishes more than twenty-five belong to this species.

(*c*) The disappearance of most of the Palæoniscidæ of the Brookvale horizon.

(*d*) The absence of the rich Sub-Holostean fauna of the Brookvale beds. At that horizon there were Catopteridæ in profusion both as individuals and as genera ; there were two genera of Perleididæ, very numerous individuals of *Macrocœthes*, and fewer but numerous specimens of *Belonorhynchus*. Yet none of these is represented in the Wianamatta, and, whereas about one hundred individuals of *Cleithrolepis* were recovered from Brookvale, comprising about one-sixth of the total collection, only two specimens are known from the St. Peter's beds.

A similar reduction of Sub-Holostean families at the close of the Mid-Triassic is to be observed on comparison of the Mid-Triassic fauna of Besano with the Upper Triassic of Perledo. The nine families of Sub-Holostei at Besano (Brough, 1939) are reduced to two at Perledo, where Holostei predominate. But these are marine deposits, which always include a richer fish fauna than do freshwater deposits of the same age.

Since the Wianamatta shales are freshwater deposits, comparison is fairly made only with other freshwater faunæ. Of these there are only two which need be considered here, namely the Upper Triassic fishes of Newark, North America, and the fishes of the Keuper Waterstones of Nottingham, England.

The Newark bony fishes are restricted to four genera, belonging to two Sub-Holostean families and one Holostean. Of these one Sub-Holostean genus (*Catopterus*) and the Holostean (*Semionotus*) make up nearly the whole fauna. From the English Keuper Smith Woodward (1890) mentions the Catopterid *Dictyopyge*, the Holostean *Semionotus*, and the indeterminable *Dipteronotus*, which resembles *Cleithrolepis* in the shape of the trunk, while Swinnerton (1925, 1928) has described the Holostean genera *Woodthorpea* and *Semionotus metcalfi*.

The substantial agreement in the nature of these assemblages with that from St. Peter's is obvious, and we may reasonably assign the latter to the early Upper Triassic.

Order HOLOSTEI.

Family PROMECOSOMINIDÆ.

Diagnosis.—Small Holostei having fusiform bodies, blunt snouts, eyes of moderate size placed centrally well above oral margin. Tail abbreviate-heterocercal, slightly forked. Cranial roof inconspicuously ornamented. Suspensorium slightly inclined forwards.

Quadrate small, triangular ; metapterygoid extensive ; endopterygoid and ectopterygoid large and irregular autopalatine small.

Nasals large, paired, meeting on midline ; frontals long ; parietals small, nearly square ; tabulars wide, triangular ; supratemporals of moderate size, irregular. circumorbitals few.

Maxillæ free, long ; supramaxillaries large ; mandible long, deep at coronoid, tapering to shallower bar anteriorly. Median gular large. Branchiostegal rays not numerous. Interoperculum small, triangular ; suboperculum roughly quadrangular ; operculum quadrangular, about same depth as suboperculum ; preoperculum deep, short, little bent forward at lower end.

Post-temporals triangular ; supra-cleithra deep, tapering ; cleithra deep, arcuate, with triangular lower ends extending forward between the mandibulæ.

Fin-rays not numerous, with long tapering proximal segments. Fulcra well developed on all fins.

Scales rhombic, thick, ganoine-covered, smooth, deepened on flanks.

Supraorbital sensory canals end back in parietals.

Remarks.—The necessity for erecting this new family will readily be seen on consideration of the following comparative summary of characters of *Promecosomina* in the description given below :

(*a*) The trunk is fairly regularly fusiform, having a nearly straight dorsal line and thus is Eugnathid in type rather than Semionotid.

(*b*) The skull roof, which has the structure normal to the Holostei in general, is more Semionotid than Eugnathid in its lack of interdigitating sutures and in the simple outlines of the constituent bones.

(*c*) The size, shape, and position relative to the suboperculum of the interoperculum is that common in the Semionotidæ, but different from that in any Eugnathid.

(d) The slight forward inclination of the suspensorium, with the accompanying very moderate bending of the preoperculum, is found in Eugnathids but not in the Semionotidæ.

(e) The mouth and dentition are intermediate in size and power between the small-mouthed Semionotids and the large-mouthed predaceous Eugnathidæ.

(f) In contrast to the small, short, forwardly placed maxilla found in all the Semionotidæ, the fishes of this family have a long maxilla, whose hinder end is on a transverse plane through the back of the orbit.

(g) *Promecosomina* has a well developed supramaxilla, a bone which is not found in Semionotids but is usual in Eugnathids and some other families.

The maxilla, viewed together with its supramaxilla, looks very like the upper jaw of *Amia calva*.

(h) In the mandible, however, as in the Semionotidæ, the coronoid tapers to its anterior segment and does not descend abruptly to it as in the Eugnathidæ.

(i) It is all but certain that the ring of circumorbitals always found in Semionotids was not present in these fishes, nor are the bones of the head arranged concentrically with the orbit as is characteristic of that family.

Promecosomina, accordingly, cannot be placed either with the Semionotidæ or with the Eugnathidæ.

In its blending of characters found separately in these two families it shows a number of points of similarity to *Parasemionotus* (Piveteau, 1934). The following are the most important points of similarity or difference :

(a) The trunks of *Parasemionotus* and of *Promecosomina* are not deepened anterior to the dorsal fin.

(b) *Parasemionotus* has a holostean skull roof, without interdigitation, and the size and shape of the bones are little different from those of corresponding bones of *Promecosomina*.

(c) A large part of the snout is covered in both genera by large paired nasals which meet in the mid-line.

(d) The opercular apparatus of both is of Semionotid type, with the difference from the Semionotidæ that in both the interoperculum does not reach far forwards.

(e) Both have a nearly vertical suspensorium.

(f) Supramaxillæ, though not of the same size or shape, occur in both genera.

(g) In both the mouth is of moderate size and the teeth sharp.

(*h*) In both the supraorbital sensory canals end far back in the parietals.

(*i*) There is, of course, a very great difference in the preopercula, the extent of which in the Parasemionotidæ is one of the characters which keep that family on the border line of the Sub-Holostei and Holostei.

It would seem, therefore, that *Promecosomina* is most probably a Holostean descendant of the very early Triassic family, Parasemionotidæ.

Promecosomina formosa (A. S. Woodward).

(Plate XVII, Text-figs. 1-3.)

1908. *Semionotus formosus*, A. S. Woodward, 1908, p. 23.
    Pholidophorus australis, A. S. Woodward, p. 26.
    Acentrophorus, A. S. Woodward, p. 21.

1935. *Promecosomina beaconensis*, R. T. Wade, 1935, p. 79.

Material and measurements :

[Let l=total length from tip of snout to base of tail ; d=maximum depth of trunk ; h=length of head to back of operculum ; cp=depth of tail at base ; lb=length of produced fleshy upper lobe of tail. All dimensions in millimetres.]

There are about twenty-seven specimens, the majority of them nearly complete fishes, in the Australian Museum, Sydney. They fall roughly into four size-groups :

(i) F. 17948 : l=210, d=68, l/d=3·1, h=58, cp=28.
    F. 38905, the type specimen of *Semionotus formosus*, which has l=144, d=43, l/d=3·3, h=38, cp=19.
    F. 17954 and F. 29729 (*b*) : l=134, d=41, l/d= 3·25, cp=18, lb=15.

(ii) F. 397 (*b*) : l=106, d=28, l/d=3·8.
    F. 29731 and F. 29718 : l=104, d=30, l/d=3·5.
    F. 29729 (*a*) : l=102, d=30, l/d=3·4.

(iii) F. 397 (*a*) : l=83, d=23, l/d=3·6, h=22.
    F. 17953 : l=82, d=22, l/d=3·7, h=20, lb=9.

(iv) F. 3196 (*b*) : l=62, d=14, l/d=4·5, h=15.
    F. 3196 (*e*) : l=60, d=14, l/d=4·3,
    F. 3196 (*d*) : l=58, d=14, l/d=4·1, h=12.
    F. 3196 (*d*) : l=56, d=13, l/d=4·5, lb=5.

(v) Nine individuals on slab No. F. 14263 and two on F. 148.

Remarks.—(A) These measurements are subject to certain errors unavoidable in dealing with material preserved as this is : (*a*) In determining l, it is usually

impossible to be sure of the exact tip of the snout, which is usually greatly crushed, or the exact base of the tail. (*b*) The fish is apt to be broken irregularly, so that one cannot be sure of exact margins. (*c*) Crushing is likely to have spread the larger fishes proportionately more than the smaller. (*d*) It is very difficult to determine the exact tip or base of the fleshy upper lobe of the tail.

(B) As the length of the fishes progressively increases, the trunks become deeper, the fishes relatively stouter; so, too, do the fin rays become stronger and distal division and jointing more frequent. Their specific identity is made certain by the following observations :

> (i) Fairly well preserved heads at each of the above four stages of growth, for example F. 38905, F. 397 (*b*), F. 17953, F. 3196 (*e*), show that the osteology of the skull was the same throughout.
>
> (ii) Although the exact number of fin rays can seldom be accurately determined, there is agreement in the kind and number of fin rays.
>
> (iii) The fins have the same relative positions.
>
> (iv) There is complete agreement in the squamation. Hence it is clear that we have a single species, any differences specimens display being due to the stage of maturity of the individuals or differences in their state of preservation.

(C) The unique originals of Plate IV, Figures 6 and 9, assigned respectively to *Acentrophorus* and *Pholidophorus* by A. S. Woodward (1908, pp. 21 and 26), are not in Australia ; but, from a comparison of the figures with individuals of like appearance in the present collection, and having in mind that they were unique specimens which yielded no information regarding the structure of the skull, the present writer considers them imperfectly preserved individuals of *Promecosomina formosa* at the same stage of maturity as, say, F. 397 (*a*) and F. 17953.

The Head.—From the present collection it is possible to compile a fuller description of the head of *Promecosomina* than the few specimens found at Brookvale supplied.

The length of the head is slightly greater than its depth at the tabulars, but is a little less than the maximum depth of the trunk.

The eye, of moderate size, is well above the oral margin, and in the anterior half of the head. The head conforms to the body contours and is neither flattened dorso-ventrally
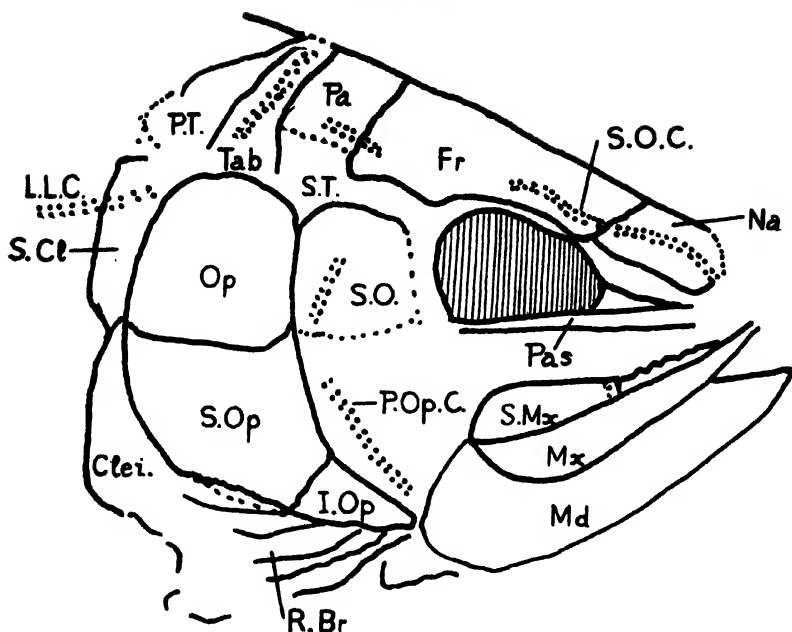
Fig. 1.

Fig. 1.—*Promecosomina formosa.* F. 38905, head slightly restored. ×7/3.
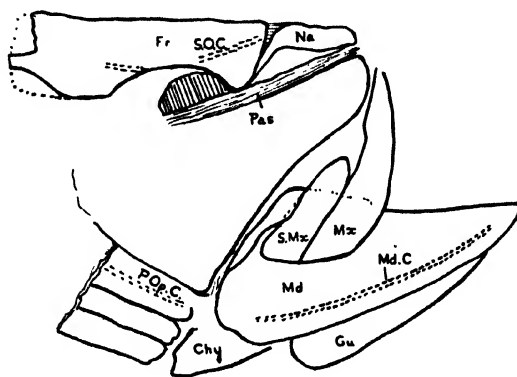
Fig. 2.

Fig. 2.—*Promecosomina formosa.* F. 17948, head. ×5/4.
Chy., ceratohyal; *Clei.*, cleithrum; *Fr.*, frontal; *Gu.*, median gular; *I.op.*, interoperculum; *L.L.C.*, lateral line canal; *Md.*, mandible; *Mx.*, maxilla; *Na.*, nasal; *Op.*, operculum;' *Pa.*, parietal; *Pas.*, parasphenoid; *P.op.C.*, preopercular canal; *P.T.*, post-temporal; *R.Br.*, branchiostegal rays; *S.cl.*, supracleithrum; *S.Mx.*, supramaxilla; *S.O.*, suborbital; *S.O.C.*, supraorbital sensory canal; *S.op.*, suboperculum; *S.T.*, supratemporal; *Tab.*, tabular.
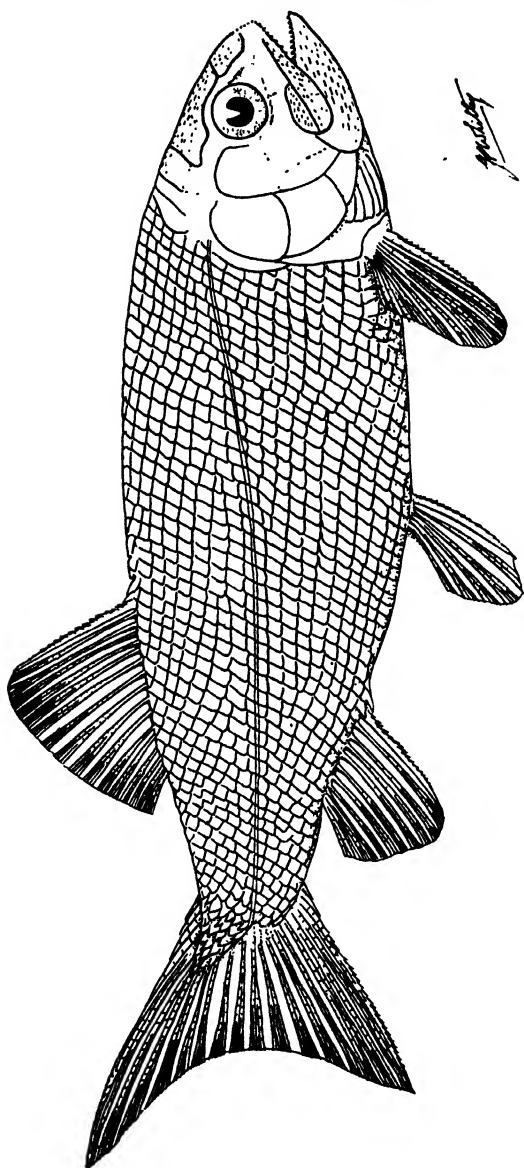
Fig. 3.

Fig. 3.—Restoration of *Promecosomina formosa*. Based on the type (F. 38905) and other specimens and drawings and descriptions by the author.

The sculpture on the maxilla and mandible should consist of longitudinal rugæ. On the frontals also there are indefinite more or less longitudinal rugæ.

nor sharp-snouted.   There is a slight ornament of irregular rugæ on the roofing bones.

In the snout, crushing prevents the determination of more than large irregular nasals, which are somewhat deeper than wide, and are deeply channelled by the sensory canal.

The frontals are long, narrow between, but widening slightly before, and more widely behind, the orbit, and have nearly straight inner margins.   The parietals which are not so well preserved, are small, paired, and nearly square.   The supraorbital sensory canals, passing back from the nasals, traverse the length of the frontals, near their outer margins, and end back in the parietals.

The tabulars, in which the supratemporal commissure of the sensory canal system is preserved either as a channel or a calcite cast, meet on the mid-line in a very short common suture, then, expanding slightly, extend behind both the parietals and supratemporals.

The latter are irregular in shape, of moderate size and width, and in U.S.G.D. 192 at least (Brookvale specimen, Wade, 1935, p. 81) bear a calcite cast of the infraorbital canal.

In few specimens is the circumorbital ring more than structureless, so that one feels sure that it did not consist of the numerous plates usual in the Semionotidæ ; for, had the bones existed, they must have left some indications of their presence in material such as this.   On the other hand, specimens F. 17953 and F. 17948 suggest that there was a large bone partly above and partly behind the orbit, with a more or less rectangular bone, much deeper than long, behind the orbit, while U.S.G.D. 192 preserves a bone below nearly the whole orbit.

A quadrangular suborbital has left its impression with moderate clearness in specimens F. 3196 (e), F. 17952, F. 17953, and less clearly in F. 38905, occupying all the space between the operculum and the circumorbital ring, and apparently overlapping the upper end of the pre-operculum.

The maxillæ are long, gently convex at the border of the mouth, and with lower margins which curve at an obtuse angle into the posterior margins.   The upper margins, at first straight anteriorly, then become gently concave.   Above nearly half of the maxilla there is a closely articulating supramaxillary bone, which is nearly as deep as the maxilla.

The black film which, in some specimens, occupies the position of the maxilla, shows only a very faint ornament of very fine longitudinal rugæ, diverging posteriorly, and more clearly to be seen on the supramaxillary (F. 38905) ; but where there is no film, longitudinal impressions are very distinct (F. 17954 and F. 397 (a)).

The mandible attains its greatest depth at about one-third of its length, after which it tapers forwards, at first very rapidly, but later more gradually.

The ornament of the underside of the mandible seems to have consisted of sparse tubercles and short rugæ, some of which branch ; its lateral impressions have longitudinal markings like those of the maxilla.

The teeth, which are well preserved in no specimen, were conical, sharply pointed, and slightly recurved, at least in the lower jaw (U.S.G.D. 192).

Some slight correction of figure 46, p. 81, Wade, 1935, is necessary ; it does not agree with the text, which states on p. 82 that the suboperculum " has a slightly produced antero-superior corner ". Re-examination of U.S.G.D. 192 confirms this and the St. Peter's material endorses it. The lower margin of the operculum is nearly straight, turning up slightly at each end. The operculum is of greater area than the suboperculum but is only slightly deeper ; except in F. 3196 (f). The interoperculum, which is small and triangular and forwardly directed, has its postero-dorsal margin extending along the whole of the corresponding margin of the suboperculum, as is usual in the Semionotidæ, not merely along a small anterior part as in the Eugnathidæ.

The front limit of the preoperculum is difficult of determination because of the well defined palatal impression, but from U.S.G.D. 192 and F. 3196 (e) we may be certain that the preoperculum was short throughout its whole depth, not greatly turned forwards at its lower end, and that, while it extended from the upper end of the operculum, its upper end was covered by the suborbital.

Regarding the palate, shoulder girdle or squamation, there is nothing here to be added to the description of those parts given in Wade, 1935, pp. 82 and 83. With reference to the supra-orbital sensory canals it should, however, be noted that it is now known that they have their hinder ends in the parietals and do not fuse with the infraorbital canals.

From specimen F. 29731, which preserves much of the endoskeleton, it is clear that there were no ossifications in the notochordal sheath. There are long, slender, neural elements, thickened proximally, extending well towards the dorsal margin, and hæmal arches or spines which are expanded beneath the caudal fin rays. Supports for the dorsal and anal fin rays are long, slightly broadened beneath the rays, which they equal in number.

II. THE RELATIONSHIPS OF THE AUSTRALIAN TRIASSIC FISHES TO EACH OTHER AND TO OTHER BONY FISHES.

In the Australian Triassic rocks, fossil fishes have been found at three horizons : at Gosford, at the top of the Lower Triassic Narrabeen shales ; at Brookvale, about six hundred feet above the base of the Mid-Triassic Hawkesbury sandstones ; and in the neighbourhood of St. Peter's, Sydney, within the Upper Triassic Wianamatta shales, at a level about five hundred feet higher than the Brookvale brick-pits.

The most completely representative of the fauna of its period is likely to be the Brookvale collection, which comprises fossils accumulated throughout twenty years, during six of which collecting was fairly intensive, while shale to a depth of about twenty-five feet was removed from about two or three acres.

The assemblage from St. Peter's, too, should be representative, for that has been gathered during a period of about forty years from a number of pits within an area of several square miles.

Collection at Gosford was made for a brief period from a band of shale less than six feet thick.

The following table shows the distribution of the fishes known from these three localities.

	Palæoniscidæ.		Sub-Holostei.			Holostei.		
	Gen.	Sp.	Fam.	Gen.	Sp.	Fam.	Gen.	Sp.
Gosford	2	3	4	7	10			
Brookvale	6	9	5	12	14	2	2	2
St. Peter's	4	6	1	1	1	1	1	1

Except for the Palæoniscidæ the course of development here agrees with that observed in marine Triassic deposits

by Brough (1939, p. 111); Sub-Holostei become dominant in the Mid-Triassic, then decrease, and are eclipsed by Holostei in the Upper Triassic.

Palæoniscidæ.

The Palæoniscidæ have different histories in marine and freshwater deposits. Whereas in the sea they declined greatly very early in the Trias, they seem to have increased in Australian Mid-Triassic waters and flourished, though not quite so abundantly, in early Upper Triassic times. But they did not go entirely unaffected by change. *Myriolepis*, it is true, is found in all Triassic localities with its known characters practically the same throughout, but *Apateolepis* has not been identified elsewhere than at Gosford, and with the exception of *Myriolepis* and possibly *Belichthys* and *Leptogenichthys*, none of the numerous Mid-Triassic Palæoniscidæ have been found in the Wianamatta shales.

Again, seeing that the Sub-Holostei are descendants of some Palæoniscid genera, it might be expected that the ancestral genetic constitution, which was such that Sub-Holostei could arise from it, would also permit some similar changes to manifest themselves in descendants which remained within the family. So it is that all the Australian Mid-Triassic genera, *Myriolepis* excepted, display modifications of the normal Palæoniscid structure.

Briefly, the more outstanding of these differences are as follows :

(1) *Agecephalichthys*. The normal Palæoniscidæ are predaceous fishes with a powerful dentition ; but fishes of this genus, though more than a yard long, have very small teeth. Their opercula, too, are only slightly, instead of greatly, deeper than their sub-opercula, and are peculiarly short in proportion to their depth.

(2) *Belichthys*. This genus, too, has opercula and sub-opercula of almost equal depth—an approach to the Catopteridæ, in which the opercula are the deeper. It also resembles some Catopteridæ in the relative shallowness of the maxilla behind the orbit.

(3) *Leptogenichthys*. This has very long jaws, and a most elaborately ornamented cranial roof.

(4) *Mesembroniscus*. The scales are so greatly deepened that only five longitudinal rows cover the whole flank— an approach to the depth attained by the scales in several Sub-Holostean families.

(5) *Megapteriscus.* A genus characterised by a great profusion of fin rays in all fins.

Summing up, the Mid-Triassic Palæoniscidæ of Brookvale exhibit variations from the normal structure of members of that family, some of the variations being excessive development of certain features such as in other forms of life may precede the extinction of a species; others approximate to characters which are found in Sub-Holostean families.

Catopteridæ.

Just as the Palæoniscidæ themselves found Australian freshwaters congenial, so too did the Catopteridæ, that family of their descendants which is most like the parent stock. It is not usual to find a family and its more highly organised issue flourishing side by side, but the reason in this case may be that the Palæoniscid genera from which the Catopteridæ sprang are not those which persist beside them.

Since the structure of the heads of the Gosford Catopteridæ cannot be determined, detailed comparison with the Brookvale species is not possible. The only observable points of difference are, first, that *Brookvalia*, which most resembles "*Dictyopyge illustrans*", or *D. robusta* in the proportions of the trunk and the nature of the squamation, has many more rays in its fins; secondly, that by the middle of the Triassic there were seven genera comprising ten species, one of which was exceedingly abundant. But the generic differences are not profound, and the most important advance from the normal structure is that *Brookvalia* and *Geitonichythys* certainly, and most probably three other genera, show convergence in the direction of the Holostei, in the fusion of the supraorbital canals with the infraorbital canals in the supratemporal bones. Outside the Holostei and Teleostei this does not occur except in the Jurassic Palæoniscid fish *Oxygnathus* (Watson, 1925).

Perleididæ.

Fishes of this family (genus *Perleidus*) were widely distributed in the earliest Triassic seas and flourished in the sea throughout the whole Triassic period.

In freshwater deposits they are found first in the Karroo beds, where *Meidiichthys browni* is the sole genus and species, but it is one of the commonest species in the

Bekker's Kraal fauna. A large proportion of the Gosford fishes belong to four genera of Perleididæ. They at once decline in kind and abundance, two genera totalling four individuals occurring at Brookvale, while none have been found at St. Peter's.

The chief advance in structure is to be found in the snouts of the Mid-Triassic genera, which are almost entirely covered by two large nasals.

Cleithrolepidæ.

Unless Oertle's *Cleithrolepsis* [*sic*] *brückneri* (1931) occurs in marine beds, the Cleithrolepidæ, like the Catopteridæ, have been found only in freshwater deposits. Their derivation from a deep-bodied ancestor such as *Platysomus* is clearly shown in the structure of the skeleton of *C. granulata* (Wade, 1935). Deep-bodied fishes, the Ecrinosomidæ or Bobasatraniidæ, lived in the Lowest Triassic seas of Greenland and Madagascar, and these must also have had deep-bodied ancestors in the Permian, but detailed comparison of the Ecrinosomidæ with *Cleithrolepis* serves only to deepen the conviction that they are derived from very different stocks. Stensiö (1932) holds that *Bobasatrania* was in the line that includes the Pycnodontidæ. Probably the Platysomidæ, though fairly uniform in general structure, are no more fundamentally homogeneous than the Palæoniscidæ from which they themselves seem to have been derived, and therefore have given rise to descendants that differ from each other.

On comparing *Cleithrolepis minor* from the Karroo beds with *C. granulata* and *C. alta*, the Australian species, some important differences are at once manifest.

(i) The dorsally angulated body of *C. minor* has become somewhat more gently curved dorsally in *C. granulata*, but more angulated and deeper in proportion to its length in *C. alta*.

(ii) The temporal region, which in *C. minor* is long and shallow, in close resemblance to the Perleididæ, has in *C. granulata* the width found in the Holostean Semionotidæ and Eugnathidæ.

(iii) The opercular apparatus, preopercula and maxillæ of the two species differ greatly in shape.

(iv) In *C. granulata* there appears a second preoperculum, probably the separated end of an original single pre-operculum, since it bears the preopercular sensory canal.

Associated, perhaps, with the separation of this second preoperculum, and the weakening at that end of the attachment of the maxilla and the support for the palate, there is developed at the lower anterior corner of the preoperculum a long sharp peg articulating with the maxilla. This possibly represents an attempt to secure a firmer support for the palate by an alternative method to that which the Holostei successfully adopted when the maxilla became "free", namely the rigid attachment of metapterygoid, preoperculum, and hyomandibula.

(v) The simple, small, triangular tabulars of *C. minor* are replaced by wide much divided tabulars in *C. granulata*.

(vi) Whereas there are few and those small branchiostegals in *C. minor*, *C. granulata* has about a dozen pairs of well developed branchiostegal rays.

(vii) The circumorbital ring of six well developed bones in *C. granulata* is much more extensive than the narrow ring of *C. minor*.

(viii) There is great difference in the shapes and relationships of the maxillæ and preopercula of the two species. In *C. minor* the suture between the two bones runs diagonally across the cheek to a point behind the orbit and is very slightly concave on the maxilla side, but in *C. granulata* the whole maxilla is well below the level of the orbit and it is the maxillæ which are hollowed to receive the preopercula.

In short, *C. granulata* presents very few points of agreement with *C. minor*—the depth of the trunk, the similar squamation, similar mandibulæ and lack of dentition. In all other respects *C. minor* is a typical Perleidid, just as in those other respects *C. granulata* is distinct from the Perleididæ. Hence we must conclude that if *C. minor* is a member of the Cleithrolepidæ, this family must have arisen from some ancestor common to both Perleididæ and Cleithrolepidæ.

Pholidopleuridæ.

Pholidopleuridæ, represented by the genus *Australosomus*, occur in the early Triassic faunas of East Greenland and Madagascar, but do not appear in Australia till the Middle Trias, where *Macrocœthes* is abundant. A third genus, *Pholidopleurus typus* Bronn, has been found at Raibl, Carinthia (Bronn, 1858; Wade, 1935), and in the marine Mid-Triassic deposits of Besano (Brough, 1939.)

Although they display a fairly uniform constitution, there are more points of agreement between *Pholidopleurus* and *Australosomus* than between *Macrocœthes* and either, possibly because *Macrocœthes* had developed in freshwaters. Detailed comparison between *Macrocœthes* and *Pholidopleurus* has already been made by the writer (Wade, 1935, p. 69), but five points of difference from the other two genera are relevant here. The first is the greater development of the gills in *Macrocœthes*, as shown by the larger opercular plates, the long series of branchiostegal rays and the presence of an opercular gill. This suggests that the habitat of this genus was not rich in oxygen, i.e. that they were bottom feeders. Secondly, there is an entire absence of teeth, replaced apparently by a rasp-like border on the maxilla. Thirdly, the scales of the hinder half of the trunk of *Macrocœthes* are so thin that they have left only the faintest impressions, whereas both *Pholidopleurus* and *Australosomus* have well developed scales over the whole trunk. *Macrocœthes*, too, has many more fin rays in its fins. Finally, while the vertebral axis of *Macrocœthes* shows no advance on that of *Australosomus*, *Pholidopleurus* has some constricted vertebræ.

On the whole we may think that *Pholidopleurus* is a more normally developed descendant of *Australosomus* than is *Macrocœthes*. Two points of seeming resemblance to higher fishes are to be found in the symmetrical tail and the presence of a backbone. The symmetry, however, is only external and is not homocercy ; the vertebral centra are rings formed in the outer tissues of the notochord itself and are intermetameric in the selachian manner.

Saurichthyidæ.

From the *Belonorhynchus* of the Gosford beds, that of Brookvale differs only in its much greater size and much smaller teeth.

Belonorhynchus, like *Macrocœthes*, displays a symmetrical, though not homocercal, tail. Further, it approaches fishes of much higher organisation in that it has bony ribs. The bony vertebral axis of the lowest Triassic *Saurichthys ornatus* (Stensiö, 1925) is not found in *Belonorhynchus gigas*.

HOLOSTEI.

The Promecosominidæ found at Brookvale and St. Peter's are of the same genus and species, but they are

much more abundant as individuals at St. Peter's. The relationship of this family to the Parasemionotidæ (Piveteau, 1934) has already been set out.

No true species of Semionotidæ occurs at the above three localities, but at Bowral a nearly normal member of the family has been found and will be described in a later paper.

It is unfortunate that the specimens of *Enigmatichthys* are so poorly preserved ; it is almost certainly as closely related to the Eugnathidæ as *Woodthorpea* (Swinnerton, 1925).

Thoracopterus (?).

An elongated pectoral fin and some scales and scattered fin rays found at Brookvale, indicating the presence there of a flying fish, are mentioned here merely for completeness of record.

SUMMARY.

(1) The known Australian Triassic fishes range from late in the Lower Trias to early in the Upper Trias ; i.e., through the period that saw the rise and fall of the Sub-Holostei.

(2) Palæoniscidæ, with characters slightly modified, flourished throughout the whole epoch.

(3) Holostei, absent in the Lower Triassic, are unimportant in the Mid-Trias, but predominate in the Upper Trias, although restricted to a single genus and species.

(4) To characters of the Sub-Holostei which converge towards those of the Holostei and which have been discussed by Brough (1936, 1939), the Australian Sub-Holostei add the following :

    (i) The development in *Cleithrolepis granulata* of a spine and socket articulation of the maxilla and preoperculum.

    (ii) The symmetrical caudal fins of *Macrœthes* and *Belonorhynchus*.

    (iii) Bony vertebræ of two types in *Macrœthes* and *Belonorhynchus*.

    (iv) The snout of *Manlietta*, in which the nasals assume the importance they have in the Holostei.

    (v) The infra-opercular plates of the Catopteridæ, which though merely modified first branchiostegal rays, represent an attempt to secure any advantage which the true interopercula confer on the Holostei.

The writer agrees with Brough in considering these and other similar modifications as the reaction to similar stimuli exhibited by fishes similar in genetic constitution to those from which *Acentrophorus* and the Parasemionotidæ were derived.

(5) *Promecosomina* is a Holostean descendant of *Parasemionotus*, *Macroæthes* a specialised freshwater Pholidopleurid, and *Cleithrolepis granulata* derived from a Platysomid stock.

Brookvalia and the other Catopteridæ comprise a group derived from a *Helichthys*-like species which entered Australian waters in the Lower Triassic, and was stimulated to variation by the local conditions.

(6) There is no Australian species which can be traced from an earlier Australian species ; the fishes all seem to have entered Australian waters in the Lower Triassic, isolation being apparently complete in Upper Triassic times.

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EXPLANATION OF PLATE XVII.

Promecosomina formosa.   F. 17948, head.   × 2.
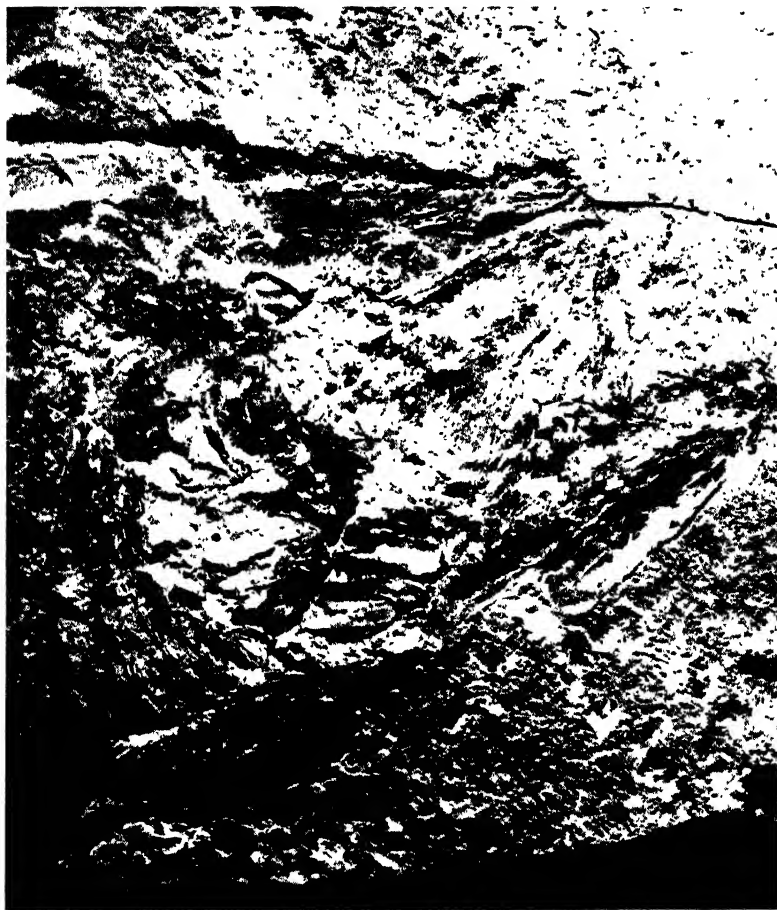
PERMIAN BRYOZOA OF EASTERN AUSTRALIA.

Part I. A Description of some Previously-named Species of Fenestrellinidæ (Fenestellidæ).

By Joan M. Crockford, B.Sc.

(With Plates XVIII-XIX and two text-figures.)

Summary.

In this paper described Permian species of *Fenestrellina*, *Protoretepora* and *Polypora* from New South Wales and Tasmania are revised from type material where that is available, or from topotypes. Neotypes are chosen for species whose holotypes are lost, and lectotypes chosen where the species was described from a series of syntypes.

Introduction.

The first record of Permian Australian Bryozoa was made by Lonsdale in 1844, when he described six new species—*Stenopora tasmaniensis, S. ovata, Fenestella ampla, F. internata, F. fossula* and *Hemitrypa sexangula*—in an appendix to Darwin's "Geological Observations on Volcanic Islands"; the specimens had been collected by Darwin from the Palæozoic formations of Van Diemen's Land. In the following year Lonsdale added to these descriptions and figured specimens from the Darwin collection in an appendix to Strzelecki's "Physical Description of N.S.W. and Van Diemen's Land", giving the localities as "Mt. Wellington, Mt. Dromedary, Van Diemen's Land"; in addition he described two new species of *Stenopora*—*S. crinita*, from the Illawarra district, N. S. Wales, and *S. informis*, from Spring Hill, Van Diemen's Land. In the main text Strzelecki records Bryozoa from other localities in New South Wales and Van Diemen's Land.

Nicholson and Etheridge state (1879, p. 273) that Darwin's type specimens of *Stenopora* are missing, and (1886, p. 173) that the Strzeleckian type only of *S. ovata* is in the British Museum; both types of *S. tasmaniensis*

are lost, and the figured *S. informis* and *S. crinita* are in the British Museum. Etheridge (1880) states that he had "endeavoured to obtain access to the types of Lonsdale's species of *Fenestella*, forming a portion of the collection formed by Dr. Darwin, F.R.S., and described in his work on 'Volcanic Islands'. Unfortunately these are not now forthcoming and appear to have been altogether lost."

Dana (1849) described two new species of *Fenestrellina, Fenestella media* and *F. gracilis* (non *Fenestella gracilis* Barrande, 1894), from Glendon, and a new species of *Stenopora* (?), *Chœtetes gracilis*, from Wollongong and Black Head, and recorded Lonsdale's species of *Fenestella* and *Stenopora* from localities in New South Wales ; the type specimen of *Chœtetes gracilis* is in the U.S. National Museum, but the specimens of *Fenestella media* and *F. gracilis* are lost, and these species cannot be recognised from the descriptions and figures given by Dana.

R. Etheridge, Snr. (1872, p. 332) records and figures *Fenestella fossula* and *Ceriopora* (?) *laxa* from the "Devonian" (now Permo-Carboniferous) of Gympie ; he states that the specimen recorded as *Fenestella fossula* was not well preserved, and that he had proposed the name *Fenestella densa* for this specimen.

de Koninck (1878) described two new genera, *Protoretepora* and *Dendricopora,* and three new species, *Fenestella propinqua, Dendricopora hardyi* and *Retepora* (?) *laxa*, and recorded Lonsdale's and several European species from Permian and Carboniferous localities in N. S. Wales ; de Koninck's specimens were destroyed in the Garden Palace fire in 1882.

Etheridge (1876, 1880, 1892) has recorded several of Lonsdale's species, and has described three new species, *Protoretepora koninckii* (1880), *Protoretepora woodsi* (1892), and *Polypora smithii* (1892), from Queensland.

Etheridge and Nicholson (1879, 1886), Nicholson (1879), and Etheridge (1891) have revised the Australian species of *Stenopora*, and described three new species, *Stenopora jackii* (1879), *S. australis* (1886) and *S. leichhardtii* (1886).

Laseron (1918) recorded Lonsdale's species of *Fenestella* and *Protoretepora*, and described six new species, *Fenestella exserta, F. cavea, Polypora pertinax, P. tumula, P. virga,* and *Protoretepora montuosa* from the Permo-Carboniferous of N. S. Wales ; the specimens figured by Laseron. (excepting that of *Polypora virga*) are in the Australian Museum Collection.

Hudleston (1883), Hinde (1890), Etheridge (1903, 1907, 1914), Bretnall (1926), and Hosking (1931), have described Western Australian species.

The distribution of the species revised, and a comparison of the measurements of specimens from the type localities, are shown in the accompanying tables.

DESCRIPTION OF SPECIES.

Family FENESTRELLINIDÆ Bassler, 1935
(FENESTELLIDÆ King, 1850).

Genus Fenestrellina d'Orbigny, 1849.

(Homonym, *Fenestella* Lonsdale, 1839, preoccupied for a pelecypod, *Fenestella* Bolton, 1798.)

Fenestrellina fossula (Lonsdale).
(Plate XVIII, Figs. 2, 3 ; text-figure 1.)

Fenestella fossula Lonsdale, 1844, in Darwin, " Geological Observations on Volcanic Islands ", p. 166.

Fenestella fossula Lonsdale, 1845, in Strzelecki, " Physical Description of N.S.W. and Van Diemen's Land ", p. 269, pl. IX, figs. 1, 1a.

Fenestella fossula (Lonsdale), Dana, 1849, " Wilkes' U.S. Exploring Expedition ", Vol. X, Geology, p. 710, pl. X, figs. 12, 13.

Fenestella fossula (Lonsdale). Etheridge, 1872, *Q.J.G.S.*, *28*, 332, pl. XXV, fig. 1.

Fenestella densa Etheridge, 1872, *Q.J.G.S.*, *28*, 332.

[Non] *Fenestella plebeia* (McCoy). de Koninck, 1878, *Mem. Soc. Roy. des Sciences de Liége*, Ser. 2, Tome VII, p. 33, pl. viii, fig. 2.

Fenestella fossula (Lonsdale). Etheridge, 1892, " Geology and Palæontology of Queensland and New Guinea ", p. 217, not pl. IX, figs. 4, 5.

Fenestella aff. *fossula* (Lonsdale). Diener, 1896, *Pal. Indica*, Ser. XV, Vol. I, pt. 2, p. 83, pls. VII, fig. 8, VIII, fig. 4.

[Non] *Fenestella fossula* (Lonsdale). Etheridge, 1907, *W.A. Geol. Surv.*, Bull. 27, p. 27, pl. VIII, figs. 11-13.

Fenestella fossula (Lonsdale). Laseron, 1918, *Jour. Roy. Soc. N.S.W.*, *52*, 193, pls. XIII-XIV.

Holotype : From " southern half of Van Diemen's Land ". (Specimen lost.)

TABLE 1.—*Distribution of Species.*

Species.	N.S.W., Lower Marine.		N.S.W., Upper Marine.							Tasmania.			
	Allandale.	Por. 132, Par. Pokolbin.	Branxton (Lower Horizon).	Branxton (Higher Horizon).	Por. 15, Par. Belford.	Por. 126, Par. Mulbring.	Stony Ck.	Ulladulla.	Bundanoon.	Marlborough.	"Southern Half of Van Diemen's Land" (Lonsdale).	Hobart District.	Kampong Apna, Timor.
Fenestrellina fossula (Lonsdale) ..	x		x	x				x		x	x	x¹	
Fenestrellina exserta (Laseron)			x	x	x	x		x					
Protoretepora ampla (Lonsdale) ..									?		x		
Polypora montuosa (Laseron)			x	x	x	x							
Polypora virga Laseron	?		x	x	x	x		x		x			
Polypora pertinax Laseron	x	x											
Polypora internata (Lonsdale) ..											x		
Polypora woodsi (Etheridge) ..				x	x	x	x	x			x	x²	?

¹ Huon Rd., Mt. Wellington (1,000 feet above sea level); Glenorchy; Margate; Grange Quarry.

² Grange Quarry.

Neotype: Sydney University Collection No. 1406. Huon Rd., Mt. Wellington, Tasmania, 1,000 feet above sea level.

Infundibuliform Fenestrellina with the celluliferous surface internal; three to four zoœcia to a fenestrule; carina with a single row of nodes.

The specimens from Huon Rd. are casts in a fine sandstone. Lonsdale states that the colony was infundibuliform with the celluliferous surface internal. There are 13 to 17 branches horizontally and 9 to 11 fenestrules vertically in 10 mm. The branches are straight, bifurcating at long intervals; increase to three rows of zoœcia generally occurs within one fenestrule before branching. The width of the branches ranges from 0·32 to 0·43 mm. (average 0·37 mm.). There is a median, usually sharply-marked carina; this

TABLE

Species.	Locality.	Branches. No. in 10 mm.	Branches. Width in mm.	...ment mm.	Zoœcia. No. of Rows.	Zoœcia. No. in 10 mm.	Zoœcia. No. per Fenestrule.	Nodes.
Fenestrellina fossula (Lonsdale).	Huon Rd., Mt. Wellington.	13 to 17	0·37	38	2	36	3 to 4	Small, 0·38 mm. apart.
Fenestrellina exserta (Laseron).	Branxton, higher horizon.	10 to 11	0·46	to 0·82	2	29	5 to 6	Small, 0·4 to 0·75 mm. apart.
Protoretepora ampla (Lonsdale)	"Southern half of Van Diemen's Land."				6		About 6·5	
Polypora montuosa (Laseron).	Branxton, higher horizon.	5 to 7	0·87 to 1·28	to 1·06	5 to 6	24	5 to 6	Large, irregularly placed.
Polypora virga Laseron.	Branxton, higher horizon.	6 to 9	0·7 to 1·08	to 0·73	3 to 4	20	4	Large, irregularly placed.
Polypora pertinax Laseron	Allandale.	8 to 12	0·48 to 0·9	19 to 0·47	3 to 4	27	4	Small, poorly developed.
Polypora internata (Lonsdale).	"Southern half of Van Diemen's Land."				3			
Polypora woodsi (Etheridge)	Stony Ck.	10 to 12	0·5 to 0·?	24 to 0 7	3	28	3 to 4	Well developed, 0·32 to 0·51 mm. apart.

CORRIGENDUM.

Page 92. Explanation to Fig. 1. *For* 8 miles to 1 inch, *read* 22 miles to 1 inch.

bears a series of rather small elongated nodes; the
distance between the nodes averages about 0·38 mm.
(0·31 to 0·48 mm.). The sides of the branches slope
outwards from the base of the carina ; the zoœcial apertures
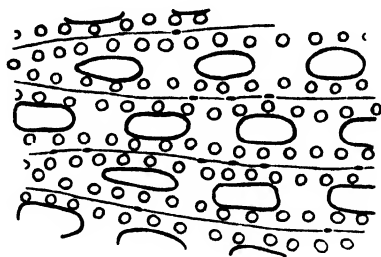
Fig. 1.—*Fenestrellina fossula* (Lonsdale), camera lucida drawing of
the celluliferous surface of the neotype.　×10.

are circular 0·16 to 0·19 mm. in diameter ; they do not
project into the fenestrules. The apertures are separated
by rather less than their own diameter the distance
between the centres of successive apertures ranging from
0·21 to 0·35 mm. (average 0·28 mm.) ; about thirty-six
apertures occur in 10 mm. and four, less often three, in
the length of one fenestrule and one dissepiment. The
fenestrules are sub-rectangular to oval, and the dissepiments
broaden slightly at their junction with the branches.
The length of the fenestrules ranges from 0·49 to 0·88 mm
(average 0·66 mm.) and their width from 0·14 to 0·35 mm.
(average 0·27 mm.). The width of the dissepiments is
from 0·16 to 0·65 mm. (average 0·38 mm.) and the
length of one fenestrule and one dissepiment is from 0·78
to 1·28 mm. (average 1·03 mm.). On the non-celluliferous
surface the dissepiments are as thick as the branches and
both are evenly rounded. The cells are rhomboidal in
outline, from 0·25 to 0·32 mm. long.

No figure accompanied the original description, but in
the following year Lonsdale, in Strzelecki, figured a
specimen from the Darwin collection.

Dana (1849) figured specimens from Glendon, N. S. Wales,
showing characters similar to those of Lonsdale's specimens.
Etheridge Snr. (1872) records and figures the species
from " Gympie, Smithfield Reef, Devonian " (now Permo-
Carboniferous) ; he states that the specimens were not well
preserved and that he at first considered them distinct,
proposing the name *Fenestella densa* for these specimens.

de Koninck (1878) listed *Fenestella fossula* Lonsdale, 1844 (together with several other species) as a synonym of *F. plebeia* McCoy, 1845 ; as Etheridge (1892) shows, his measurements would not include *F. fossula* ; he recorded the species from the Carboniferous of Glen William.

Etheridge (1892) figured a specimen showing two zooecia to a fenestrule as *Fenestella fossula*, but stated in the description that there are three or four zooecial apertures to a fenestrule ; his specimens were from Gympie, Rockhampton and the Bowen River coalfield. Etheridge (1907) recorded and figured a larger species as *Fenestella fossula* from the Irwin R., West Australia. Laseron (1918) figured as *Fenestella fossula* a specimen from Branxton which shows measurements agreeing very closely with those of specimens from Tasmania.

Remarks : Fenestella jabiensis Waagen and Pichl, 1887, from the Upper and higher Middle Productus Limestone, is separated from *Fenestrellina fossula* by its more numerous nodes, placed in a double line along the carina. *Fenestella affluensa* Bretnall, 1926, from the Callytharra stage, W.A., is apparently separated from this species only by the absence of a carina and nodes.   From *Fenestella spinulifera* Moore, 1929, which shows the same number of zooecia to a fenestrule, and similar nodes and carina, this species is distinguished by its larger size.   *Fenestella modesta* Ulrich, 1880, is slightly smaller and shows rather fewer zooecia to a fenestrule. *Fenestella modesta* and *F. spinulifera* have both been recorded from the Callytharra stage of Western Australia.

Fenestrellina exserta (Laseron).

Fenestella exserta Laseron, 1918, *Jour. Roy. Soc. N.S.W.*, 52, 195, pl. 7, figs. 1, 2, pl. 12.

Fenestella cavea Laseron, 1918, *Jour. Roy. Soc. N.S.W.*, 52, 197, pls. 15, 16.

Lectotype : Australian Museum Collection, F. 20199 (Laseron, 1918, pls. VII, fig. 1, XII, fig. 1) ; Railway Cutting, Branxton, N. S. Wales ; Fenestella shales, Higher Horizon.

Fenestrellina with five to six zooecia to a fenestrule ; apertures exserted ; slight carina with poorly developed nodes.

The form of the zoarium is not shown, but it was probably flabellate ; specimens range up to five inches in length.

There are from 5·5 to 6 fenestrules vertically, and 10 to 11 branches horizontally, in 10 mm. The branches are straight, 0·32 to 0·56 mm. (average 0·46 mm.) in width, and show a median sharp carina separating the two rows of zooecial apertures. Nodes are poorly developed and are from 0·39 to 0·74 mm. apart. The apertures are circular, 0·11 to 0·14 mm. in diameter; they are frequently closed by a calcareous plate and are raised above the surface of the branch. There are five apertures in the length of each fenestrule, with often an extra aperture opposite the dissepiment; the apertures are separated by about twice their own diameter, the distance between the centres of successive apertures being from 0·29 to 0·48 mm. (average 0·34 mm.); about twenty-nine apertures occur in 10 mm. The fenestrules are rectangular in outline, 1·16 to 1·93 mm. (average 1·58 mm.) in length and 0·32 to 0·58 (average 0·44 mm.) in width; the dissepiments are from 0·17 to 0·82 mm. in width, and the length of one fenestrule and one dissepiment ranges from 1·37 to 2·12 mm. (average 1·79 mm.). On the celluliferous surface the dissepiments may show a faint ridge parallel to their length. On the reverse surface both branches and dissepiments are evenly rounded. The branches are about 0·2 mm. in thickness and the dissepiments not quite so thick. Bifurcation occurs at intervals of 2 cm. or more; increase to three rows of zooecia occurs generally within one fenestrule before bifurcation.

Laseron described *Fenestella exserta* and *F. cavea* from the same horizon at Branxton. The most important differences between them were the number of zooecia to a fenestrule— four to five in *F. exserta*, usually six in *F. cavea*—and the form of the carina, which in *F. exserta* was faint and sinuous and in *F. cavea* was low, but showed vertical walls and was very distinct. In *F. exserta* the zooecial apertures were raised above the surface of the branch. The length of the fenestrules in *F. exserta* is given as 1 mm. and in *F. cavea* as 1 to 1·5 mm.; *F. exserta* showed six and *F. cavea* six to seven fenestrules in 10 mm. Figures are given of both species, and the magnification is given as the same for each species. The magnifications given for *F. exserta* on pl. VII do not agree with those on pl. XII, and the species is larger than appears from the figures given. These species could not be separated by any difference in their measurements, and the appearance of their surfaces suggests that *F. exserta* is unweathered and *F. cavea* is a slightly weathered form.

Remarks : *Fenestrellina plebeia* McCoy and *F. placida* Moore are similar species ; it is probable that this is the species recorded by McCoy in 1847 as *F. plebeia ?*, from Korinda. From *F. propinqua* de Koninck this species is, as Laseron has noted, distinguished by the number of zoœcia to a fenestrule, and by its more regular growth.

Genus **Protoretepora** de Koninck.

Genotype : *Fenestella ampla* Lonsdale.

Fenestrellinidœ in which zoœcia occur on both branches and dissepiments ; branches with more than two rows of zoœcia.

Protoretepora de Koninck, 1878, was proposed for infundibuliform Fenestellids in which the whole internal surface is covered with numerous rows of small cells ; de Koninck states that "*Fenestella ampla* Lonsdale may be considered the type ". He distinguished *Protoretepora* from *Retepora* because the apertures are on the internal surface and the cells are more closely packed ; from *Polypora* by the presence of cells on the cross-bars ; and from *Synocladia* by the absence of small keels separating the rows of apertures, and by its more rounded fenestrules.

Lonsdale's figures of specimens of *Fenestella ampla* from the Darwin Collection (in Strzelecki, 1845, pl. IX) include two forms—Figure 3*b*, showing additional zoœcia on the dissepiments, with no non-cellular dissepimental tissue developed, and Figures 3, 3*a*, and 3*c*, showing no extra zoœcia on the dissepiments, although the apertures of the lateral rows may encroach on the ends of the dissepiments, and differing from Figure 3*b* also in the number of zoœcia to a fenestrule and in the shape of the fenestrules. The first of these species is similar to *Phyllopora cribellum* de Koninck and *P. jabiensis* Waagen and Pichl from the Salt Range ; these however differ from the type of *Phyllopora* both in having more than two rows of cells (Bassler, 1929, p. 82) and in the celluliferous surface being internal instead of external in *Phyllopora cribellum* (the form of the zoarium in *Phyllopora jabiensis* is not known). The second species is possibly identical with *Polypora montuosa* (Laseron), and differs from the type species of *Polypora* in the form of the zoarium—infundibuliform with the celluliferous surface internal, instead of flabellate.

de Koninck did not differentiate between these two species, and the species which he described as *Fenestella*

ampla Lonsdale is distinct, and was named *Protoretepora ampla* var. *woodsi* by Etheridge (1892); specimens of this species from Stony Creek (Homeville) do not show celluliferous dissepiments.

de Koninck's diagnosis of *Protoretepora* applies most closely to the species figured by Lonsdale, 1844, pl. IX, fig. 3*b*; not 3, 3*a*, 3*c*, to which the name *Protoretepora ampla* is here restricted.

Etheridge (1892) states that *Protoretepora* differs from *Polypora* in the absence of a well-defined separation into branches and dissepiments, and in the whole of the internal surface being celluliferous, and in the form of the colony; the form of the colony distinguished *Protoretepora* from *Phyllopora*, but this character alone has not been shown to be of generic value. Among the differences listed by Laseron (1918) are that the striæ of the non-celluliferous surface are concentric in *Protoretepora* and longitudinal in *Polypora*, and that the celluliferous surface shows rhomboidal ridges in *Protoretepora* and not in *Polypora* (both these distinctions are due to weathering of the surface of the zoarium); also that the cells are rhomboidal in *Protoretepora* and oval with thicker walls in *Polypora*— these differences depend on the level at which the zoarium is cut—and that the ranges of cells are diagonal in *Protoretepora* and longitudinal in *Polypora*; he did not consider that cells always occurred on the dissepiments in *Protoretepora*, but believed that the form of the colony was important.

Remarks: *Protoretepora* de Koninck is distinguished from *Polypora* McCoy by the presence of zoœcia to the exclusion of dissepimental tissue on its dissepiments; from *Synocladia* King by its straight dissepiments, and the absence of anastomosis between the dissepiments; and from *Phyllopora* King by the presence of more than two rows of cells on the branches. The majority of the species described as *Phyllopora* should be referred to *Protoretepora*.

<div align="center">

Protoretepora ampla (Lonsdale).

(Pl. XIX, Fig. 4; text-figure 2.)

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Fenestella ampla Lonsdale, 1844, in Darwin, Geol. Obs. on Volc. Is., p. 163.

Fenestella ampla Lonsdale, 1845, in Strzelecki, Phys. Descr. N.S.W. and Van Diemen's Land, pp. 87, 94, 95, 96, 268, pl. 9, fig. 3*b*, not figs. 3, 3*a*, 3*c*.

[Non] *Fenestella ampla* (Lonsdale).   Dana, 1849, Wilkes'
U.S. Exploring Expedition, Vol. X, Geology, p. 710,
pl. 11, figs. 1, 1a.

[Non] *Polypora ampla* (Lonsdale) sp.   Etheridge, 1876,
Trans. Roy. Soc. Vic., *12*, 66, figs. 1, 1a.

[Non] *Protoretepora ampla* Lonsdale.   de Koninck, 1878,
Mem. Soc. roy. des Sciences de Liége, Ser. 2, Tome VII,
p. 42, t. 8, f. 5a-c.

[Non] *Protoretepora* cf. *ampla* Lonsdale.   Etheridge, 1880,
Proc. Roy. Phys. Soc. Edinb., *5*, 16.

[Non] *Protoretepora ampla* Lonsdale.   Lyddecker, 1883,
Mem. Geol. Surv. India, *22*, 159, pl. II, fig. 1.

Protoretepora ampla Lonsdale.   Etheridge, partim, 1892,
"Geology and Palæontology of Queensland and New
Guinea", p. 221.

[Non] *Protoretepora ampla* Lonsdale.   Diener, 1896, *Pal.
Indica*, Ser. XV, *1*, pt. 2, p. 85, pl. VII, fig. 10, pl.
VIII, figs. 1-2.

[Non] *Protoretepora ampla* Lonsdale.   Diener, 1903, *Pal.
Indica*, Ser. XV, *1*, pt. 5, p. 158.

[Non] *Protoretepora ampla* Lonsdale.   Laseron, 1918,
Jour. Roy. Soc. N.S.W., *52*, 189, pl. 4.

[Non] *Protoretepora ampla* Lonsdale.   Bion, 1928, *Pal.
Indica*, N.S., *12*, pp. 35, 39, 42.

[?] *Protoretepora ampla* Lonsdale.   Reed, 1932, *Pal. Indica*,
N.S., *20*, No. 1, p. 12.

Holotype : Lost ; from southern half of Tasmania.

*Infundibuliform with the celluliferous surface internal (?) ;
zoœcia in six rows on the branches, with about 6·5 in the
length of one fenestrule and one dissepiment ; extra zoœcia
covering each dissepiment.*

No material of this species from Tasmania is available
for description. Specimens from Bundanoon of a form
closely resembling that figured in Strzelecki show that the
zoarium is infundibuliform, with the celluliferous surface
internal, and the colony may reach a height of two inches
and a width of four inches ; the upper margin is very
much folded ; there are 6 to 8 branches in 10 mm. hori-
zontally, and 4·5 to 5 fenestrules in 10 mm. vertically.
The branches are flattened on the celluliferous surface ;
the zoœcial apertures do not project into the fenestrules.
The branches are about 0·89 to 0·99 mm. wide.   The

fenestrules are rounded, from 0·77 to 0·97 mm. long and
from 0·54 to 0·8 mm. wide ; the dissepiments are from
1·15 to 1·45 mm. wide, the length of one fenestrule and
one dissepiment ranging from 1·9 to 2·4 mm. The
dissepiments broaden considerably where they meet the
branches, and, as the whole of the internal surface is
celluliferous, the division into branches and dissepiments
is poorly defined, and shown chiefly by the direction of
the longer diameter of the cells and of the fenestrules, and
the direction of bifurcation. Each branch shows normally
four to five rows of zoœcial apertures, increasing to six to
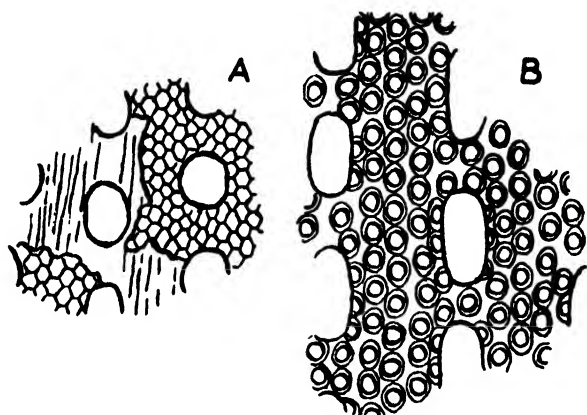
Fig. 2.—Figures of *Protoretepora ampla* (Lonsdale) given by Lonsdale
(in Strzelecki, 1845, pl. IX). A. Fig. 3*b*, with dissepiments
covered by zoœcia. B. Fig. 3*c*, showing dissepiments without
extra zoœcia.

eight before bifurcation ; the dissepiments each show about
two extra rows. There are three zoœcia opposite each
fenestrule, with an extra three opposite each dissepiment.
The cells are rhomboidal in outline on the flat basal plate.
The apertures are circular, about 0·18 mm. in diameter
and are frequently closed by a centrally-perforated cal-
careous plate ; the peristomes are fairly broad but not very
high. The distance between the centres of successive
apertures is from 0·37 to 0·5 mm., and about twenty-five
apertures occur in 10 mm. The apertures of adjacent
rows are very close together, so that the greater part of
the celluliferous surface is covered by the apertures and
peristomes. No nodes are shown. On the reverse surface
both branches and dissepiments are rounded, and are of

about the same thickness. The normal thickness of the
branches is about 0·4 mm., but near the base of the colony
extra thickening covers over the apertures and fills in the
fenestrules, and the thickness of the branches is up to
1·5 mm. The reverse surface is finely granular ; the
inner layers show faint longitudinal striæ.

Remarks : Specimens recorded as *Protoretepora ampla*
from eastern Australia by Dana (1849), Etheridge (1876,
1880), and Laseron (1918) differ from this species in the
absence of cells on the dissepiments, and in the number of
rows of zoœcia and the number of zoœcia to a fenestrule ;
figures given by Diener (1896) (using specimens from the
Zéwan beds of Kashmir figured by Lydekker in 1883)
show more zoœcia to a fenestrule (eight instead of six).
Bion (1928) recorded specimens from Kashmir identical
with those described by Diener. Reed (1932) recorded as
Protoretepora ampla specimens from Kashmir having zoœcia
on the dissepiments, and states that they were probably
identical with those figured by Diener.

Genus Polypora McCoy.

Polypora montuosa (Laseron).
(Pl. XVIII, Fig. 4 ; Pl. XIX, Fig. 2.)

Protoretepora montuosa Laseron, 1918, *Jour. Roy. Soc.
N.S.W.*, 52, 187, pls. I, II, III, fig. 2.

? Fenestella ampla Lonsdale, 1845, in Strzelecki, Phys.
Descr. N.S.W. and Van Diemen's Land, p. 268,
pl. IX, figs. 3, 3c ; not fig. 3b.

Lectotype : Australian Museum Collection, F. 20191
(Laseron, 1918, pls. I, II, III, fig. 2) ; Railway cutting,
1 mile west of Branxton, N. S. Wales ; Fenestella Shales,
Higher Horizon.

*Infundibuliform Polypora, with five to six rows of zoœcia
and almost five to almost six zoœcia in the length of one
fenestrule and one dissepiment.*

The colony is infundibuliform, with the celluliferous
surface internal ; there are four to four and a half fenestrules
in 10 mm. vertically, and five to seven branches in 10 mm.
horizontally. The branches are rounded on the celluliferous
surface and the lateral rows of apertures project into the
fenestrules and encroach on the ends of the dissepiments ; the
zoœcia themselves are normally restricted to the branches
(Laseron, 1918, pl. III, fig. 2) and extra zoœcia rarely occur ;

the zoœcia are rhomboidal in outline on the basal plate. The number of rows of zoœcia is six to eight before, and three to four after, bifurcation ; normally there are five to six rows.   The apertures are circular, with well-marked peristomes, and are from 0·14 to 0·16 mm. in diameter ; they are separated by about twice their own diameter, the distance between the centres of successive apertures being from 0·36 to 0·51 mm. (average 0·41 mm.) ; about twenty-four apertures occur in 10 mm.   Nodes occur generally along the mid-line of the branches.   The branches are from 0·87 to 1·08 mm. in width where there are four, and 1·14 to 1·28 mm. where there are five rows of zoœcia ; before bifurcation this increases to 1·4 mm. where there are six, and 2·2 mm. where there are eight rows ; where three rows occur after bifurcation the width is about 0·81 mm.   The fenestrules are oval on the celluliferous surface, from 1·13 to 1·75 mm. in length and 0·43 to 0·86 mm. in width ; the dissepiments are from 0·51 to 1·06 mm. in width, and the length of one fenestrule and one dissepiment is from 1·90 to 2·82 mm.   On the reverse surface the dissepiments are generally slightly less thick than the branches ; both are rather sharply convex, except before bifurcation, when the backs of the branches become very much flattened. The branches are about 1·8 mm. thick.   The fenestrules appear oval on the reverse side.   The outermost layer on both surfaces is finely granular ; the next layer of the non-celluliferous surface shows fine striæ concentric with the edges of the fenestrules ; beneath this the striæ are restricted to the branches.   The celluliferous surface shows, when worn, ridges and grooves swinging around the apertures.   Bifurcation occurs usually within 2 cm.

Since the dissepiments are not normally celluliferous this species is here referred to *Polypora* instead of *Protoretepora*.

Remarks :   The reverse surface of *Polypora woodsi* Etheridge resembles this species, but is distinguished by its much smaller size.   From *Polypora transiens* Waagen and Pichl (Middle Productus Ls., Salt Range) this species is distinguished by its rather smaller size, and by the characters of the celluliferous surface.

Polypora virga Laseron.
(Pl. XIX, Fig. 3.)

Polypora virga Laseron, 1918, *Jour. Roy. Soc. N.S.W.*, 1918, Vol. LII, p. 192, pl. VII, fig. 4, pl. VIII, fig. 2.

Non *Polypora virga* Tolmatchoff, 1924, Faune du calaire carbonifere du bassin houilles de Kousnetck, *Matér. Com. Geol. Leningrad,* No. 25, pl. I, p. 277.

Holotype : Lost.

Neotype : Sydney University Collection, No. 1407 ; Railway cutting, 1 mile west of Branxton, N. S. Wales ; Fenestella Shale, Higher Horizon.

Polypora with three to four rows of zoœcia, and four zoœcia to a fenestrule ; nodes large, infrequently developed.

There are 6 to 9 branches horizontally, and 4·5 to 5 fenestrules vertically in 10 mm. The branches are flattened on the celluliferous surface and show three (less often four) rows of apertures ; there are two to three rows immediately after, and four to five rows before, bifurcation. The branches are 0·70 to 0·81 mm. wide where there are three rows of apertures, 0·87 to 1·08 mm. with four, about 1·3 mm. with five, and 0·5 to 0·6 mm. with two rows. Bifurcation occurs usually within 1 to 3 cm. There are four apertures in the length of one fenestrule and one dissepiment ; the apertures are sub-circular, 0·24 to 0·28 mm. in diameter, and are separated by about their own diameter, the distance between the centres of successive apertures ranging from 0·41 to 0·57 mm. (average 0·51 mm.) ; there are about twenty apertures in 10 mm. ; the apertures are frequently closed. High nodes infrequently occur ; where there are two rows of apertures these are separated by a sharp ridge on which the nodes are placed. The cells are rhomboidal in outline on the basal plate, which is markedly convex towards the reverse surface. The fenestrules are rectangular to slightly oval, 1·30 to 1·87 mm. in length and 0·24 to 0·8 mm. in width ; the dissepiments expand only slightly at their junction with the branches ; they are from 0·30 to 0·73 mm. in width, and the length of one fenestrule and one dissepiment ranges from 1·90 to 2·23 mm. On the reverse surface the branches are thicker than the dissepiments ; both are evenly rounded. The outermost granular layer may become very thick ; the mid-line of the reverse surface of the branches shows irregular small tubercles placed rather close together. The striated layers show about twelve longitudinal striæ.

Remarks : Polypora virga is distinguished from *P. tumula* and *P. pertinax* by its larger size and by the characters of the celluliferous surface.

Polypora pertinax Laseron.

(Plate XVIII, Fig. 5.)

Polypora pertinax Laseron, *Journ. Roy. Soc. N.S.W.*, 1918, *52*, 190, pls. V, VI, VIII, fig. 1, X, fig. 1.

Lectotype : Australian Museum Collection, F. 20188 (Laseron, 1918, pl. V, fig. 2, pls. VII, VIII, fig. 1) ; Railway cutting, Allandale, N. S. Wales ; above *Eurydesma cordatum* Horizon.

Flabellate Polypora, with three to four rows of zoœcia, and four zoœcia to one fenestrule and one dissepiment ; nodes poorly developed.

The zoarium is flabellate, with four initial branches. There are 8 to 12 branches horizontally, and 7 to 9 fenestrules vertically in 10 mm. Each branch shows generally three (less often four) rows of zoœcial apertures ; there are five to six rows before, and two to three rows after, bifurcation. The branches are flattened on the celluliferous surface, and are from 0·48 to 0·73 mm. (average 0·62 mm.) in width where there are three rows of apertures, about 0·43 mm. where there are two, and from 0·66 to 0·95 mm. where there are four rows. Bifurcation may occur within 1 cm. but is usually less frequent. Faint ridges separate the rows of apertures ; these are more marked when the specimen is worn, or where only two rows of zoœcia occur. Small nodes are infrequently developed between the rows of apertures ; four may surround each aperture in the mid-line. In the central row there are three apertures opposite each fenestrule with an extra one opposite each dissepiment ; three or four apertures occur in the same distance in the lateral rows. The apertures are circular, about 0·16 to 0·17 mm. in diameter ; they are separated by rather more than their own diameter, the distance between the centres of successive apertures ranging from 0·29 to 0·43 mm. (average 0·37 mm.). There are twenty-seven apertures in 10 mm. The peristomes are well marked. The fenestrules are sub-rectangular in outline and are from 0·81 to 1·31 mm. (average 1·03 mm.) long and from 0·19 to 0·52 mm. (average 0·33 mm.) wide ; the dissepiments are rounded on the obverse surface and from 0·19 to 0·47 mm. (average 0·35 mm.) wide. The length of one fenestrule and one dissepiment is from 1·3 to 1·65 mm. (average 1·38 mm.). The dissepiments broaden slightly at their junction with the branches ; where they are worn they show strong

transverse striæ on both surfaces. On the reverse surface the dissepiments are not quite so thick as the branches; the dissepiments are rounded and the branches flattened. The outermost granular layer is generally worn away on this surface, and the outer striated layer, showing about twelve longitudinal striæ, is shown.

Remarks : Polypora pertinax shows the same length of fenestrule, width of dissepiment, number of rows of zoœcia, and number of zoœcia to a fenestrule as *Polypora tripliseriata* Bassler, from the Bitauni beds of Timor; the zoœcial apertures are rather more widely spaced (0·37 mm. instead of 0·31 mm.) and the branches are wider and fenestrules narrower in *Polypora pertinax.* From *Polypora tumula* Laseron it is distinguished by its poorly-developed nodes, and by the characters of the reverse surface. From *Polypora elliptica* Rogers it is distinguished by its larger size.

Polypora internata (Lonsdale).

Fenestella internata Lonsdale, 1844, in Darwin, Geol. Obs. on Volc. Is., p. 165.

[Non] *Fenestella internata* Lonsdale, 1845, in Strzelecki, Phys. Descr. N.S.W. and Van Diemen's Land, p. 269, pl. 9, figs. 2, 2a.

[?] *Fenestella internata* (Lonsdale). Dana, 1849, Wilkes' U.S. Expl. Exped., Vol. X, Geology, p. 710, pl. 10, figs. 13, 13a.

[Non] *Fenestella internata* (Lonsdale). de Koninck, 1878, *Mem. Soc. roy. des Sciences de Liége*, Ser. 2, Tome VII, p. 38.

[Non] *Fenestella internata* (Lonsdale). Etheridge, 1892, Geology and Palæontology of Qld. and New Guinea, p. 218, pl. 9, figs. 6, 7.

[Non] *Fenestella* sp. aff. *internata* (Lonsdale). Diener, 1896, *Pal. Indica*, Ser. XV, *1*, pt. 2, p. 84, pl. VII, fig. 9, pl. VIII, fig. 3.

[Non] *Fenestella internata* (?) (Lonsdale). Laseron, 1918, *Jour. Roy. Soc. N.S.W., 52*, 194, pl. 10, fig. 2, pl. 11.

Holotype : Lost. From " southern half of Van Diemen's Land " (Lonsdale, in Darwin).

No figure accompanies the original description given by Lonsdale (in Darwin, 1844, p. 165), which is insufficient for identification of the species, but from the detailed

description given of the bifurcation of the branches it is clear that the form described was a *Polypora* with, normally, three rows of zoœcia.

In 1845 Lonsdale (in Strzelecki) recorded the species from localities in New South Wales and Tasmania; a figure is also given, but is not of a specimen from the Darwin collection. The figure is of a species of *Fenestrellina* and does not agree with the original description.

In 1845 Lonsdale (in Strzelecki) gives the locality for the species as " Mt. Wellington; Van Diemen's Land; St. Patrick's Plains, Raymond Terrace, N.S.W." Dana (1849) recorded and figured *Fenestella internata* from Glendon; an enlarged figure shows three rows of zoœcia. de Koninck (1877) recorded but did not figure the species from the Karua River (Carboniferous). Etheridge (1892) recorded and figured this species from Stanwell, Queensland; the figures show two rows of zoœcia and three to four zoœcia to a fenestrule. Laseron (1918) figures the non-celluliferous surface of a specimen of *Fenestrellina* from Allandale as *Fenestella internata*.

Polypora woodsi (Etheridge).
(Pl. XVIII, Fig. 1; Pl. XIX, Fig. 1.)

Protoretepora ampla (Lonsdale). de Koninck, 1878, *Mem. Soc. roy. des Sciences de Liége*, Ser. 2, Tome VII, p. 42, t. 8, f. 5*a-c*.

Non *Fenestella ampla* Lonsdale, 1844, in Darwin, Geol. Obs. on Volc. Is., p. 163.

Protoretepora sp. indet. Etheridge, 1880, *Trans. Roy. Phys. Soc. Edinb.*, *5*, 16.

Protoretepora ampla var. *woodsi* Etheridge, 1892, "Geology and Palæontology of Queensland and New Guinea ", p. 222, pl. 8, fig. 12.

Polypora tumula Laseron, 1918, *Jour. Roy. Soc. N.S.W.*, *52*, 191, pl. VII, fig. 3, IX.

? Polypora tripliseriata Bassler, 1929, Palæontologie von Timor, XXVIII, p. 79, pl. CCXLII (18), figs. 14-16.

Holotype: Destroyed in Garden Palace Fire, 1882.

Neotype: Sydney University Collection, No. 1408; Railway cutting near junction of Por. 26, Par. Gosforth, and Por. 65, Par. Maitland (Stony Ck.), N. S. Wales; Fenestella Shales.

Infundibuliform Polypora with the celluliferous surface internal; three rows of zoœcia, with three to four zoœcia to a fenestrule; nodes strongly developed.

The colony is infundibuliform with the celluliferous surface internal; there are from ten to twelve branches horizontally, and eight fenestrules vertically in 10 mm. The branches normally show three rows of zoœcial apertures; there are four to five rows before, and two to three rows after bifurcation. Nodes are well developed, from 0·32 to 0·51 mm. apart; four large nodes surround each aperture in the mid-line. The apertures are circular, 0·16 mm. in diameter, and are not raised above the general surface of the branch; they are separated by about their own diameter, the distance between the centres of successive apertures being from 0·29 to 0·48 mm. (average 0·36 mm.); about twenty-eight apertures occur in 10 mm. There are three apertures in the length of each fenestrule, and an extra one may occur opposite the dissepiment; the lateral rows of zoœcial apertures do not usually project into the fenestrules, and zoœcia do not occur on the dissepiments. The branches are from 0·52 to 0·63 mm. wide where there are three rows of apertures, and about 0·8 mm. where there are four, or 0·38 mm. where there are two rows. The fenestrules are oval, 0·76 to 1·25 mm. (average 0·92 mm.) in length and 0·27 to 0·48 mm. in width; the dissepiments are from 0·24, to 0·70 mm. (average 0·41 mm.) in width, and the length of one fenestrule and one dissepiment is from 1·14 to 1·6 mm. (average 1·33 mm.). On the non-celluliferous surface the dissepiments are not quite so thick as the branches. The specimens from the type locality are preserved in casts in a coarse brown sandstone.

Specimens of this species from the higher horizon of the Fenestella shales at Branxton, including Laseron's specimens of *Polypora tumula*, show from 9 to 12 branches horizontally, and 6·5 to 8 fenestrules vertically in 10 mm. The fenestrules are from 0·79 to 1·19 mm. (average 0·99 mm.) in length and from 0·22 to 0·68 mm. (average 0·43 mm.) in width; the width of the dissepiments is from 0·22 to 0·56 mm. (average 0·40 mm.) and the length of one fenestrule and one dissepiment is from 1·11 to 1·71 mm. (average 1·38 mm.). Where there are three rows of zoœcia the branches are from 0·59 to 0·71 mm. wide; this increases to about 0·9 mm. where there are four, or 1·13 mm. where there are five rows, and is about

0·45 where there are two rows. The distance between the centres of successive zooecial apertures averages 0·38 mm. (0·30 to 0·46 mm.). Bifurcation occurs at intervals of about 2 cm. but may be much more frequent; normally increase to four, then five rows of zooecia occurs within two fenestrules before bifurcation. Where there are two rows after bifurcation increase to three rows occurs within four fenestrules. On the reverse surface both branches and dissepiments are steeply convex, and are about the same thickness; at the junction of each branch and dissepiment there is a well marked tubercle.

Remarks : *Polypora woodsi* is distinguished from *P. pertinax* by the appearance of the celluliferous and reverse surfaces, and by the number of rows of zooecia, which may be four in *P. pertinax*. From *Polypora hexagona* Moore it is distinguished by showing three, not four, rows of apertures. This species is probably identical with *Polypora tripliseriata* Bassler from the Btiauni beds (Paleo-Dyas) of Timor.

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EXPLANATION OF PLATES.

PLATE XVIII.

Fig. 1.—*Polypora woodsi* (Etheridge). Reverse surface of a specimen from the higher horizon in Branxton Railway Cutting.   ×10.

Fig. 2.—*Fenestrellina fossula* (Lonsdale). Reverse surface of a topotype weathered to show the backs of the cells.   ×10.

Fig. 3.—*Fenestrellina fossula* (Lonsdale). Cast of the celluliferous surface of the neotype.   ×10.

Fig. 4.—*Polypora montuosa* (Laseron). Topotype showing the form of the colony.   ×2.

Fig. 5.—*Polypora pertinax* Laseron. Topotype showing the form of the colony.   ×2.

PLATE XIX.

Fig. 1.—*Polypora woodsi* (Etheridge). Neotype.   ×2.

Fig. 2.—*Polypora montuosa* (Laseron). Celluliferous surface of a topotype.   ×10.

Fig. 3.—*Polypora virga* Laseron. Reverse surface of the neotype.   ×10.

Fig. 4.—? *Protoretepora ampla* Lonsdale. Reverse surface of a specimen from Bundanoon weathered to show the base of the cells.   ×16.
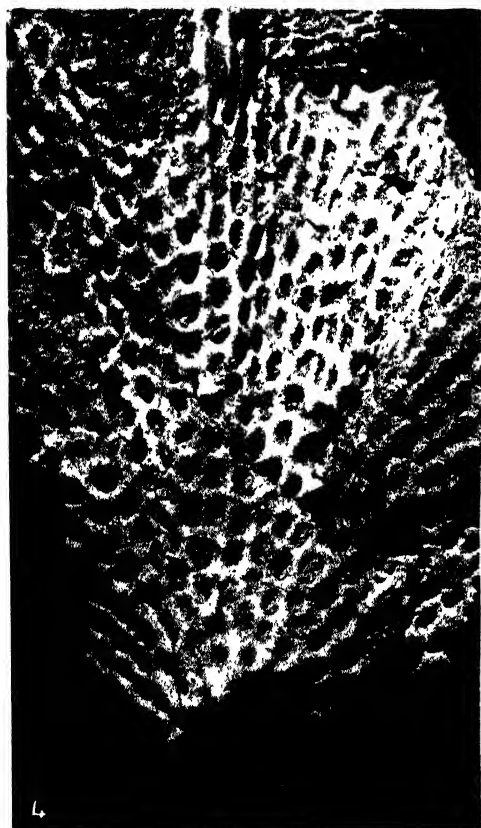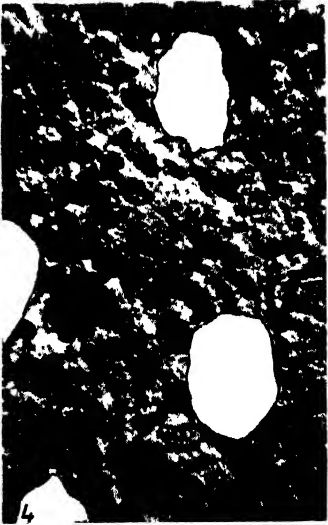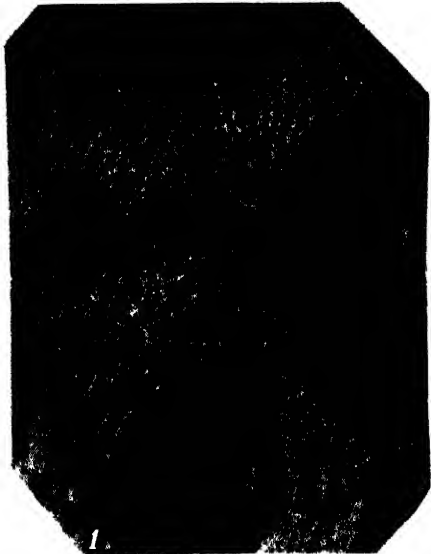
A NOTE ON SOME LEUCITE-BEARING ROCKS FROM N.S.W., WITH SPECIAL REFERENCE TO AN ULTRABASIC OCCURRENCE AT MURRUMBURRAH.

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I. Introduction and Previous Records.

Occurrences of leucite-bearing rocks described under the general term of leucite-basalts have been recorded from several isolated districts in N. S. Wales.   T. W. E. David and J. Milne Curran discovered leucite-bearing rocks near Byrock almost simultaneously.   David forwarded his specimen to Judd,[20] who recorded it as the first discovery of leucite in Australia.   In the same year Curran[8] published a note on this occurrence and referred also to the discovery of similar rocks about 50 miles to the south of El Capitan.   Later David and Anderson,[11] who had accompanied Curran to El Capitan, described and figured specimens from both Byrock and El Capitan.   In 1891 Curran[9] described two specimens of " leucite-basalt " from between Harden and Murrumburrah, and in this communication he expressed the opinion that the rock occurred as a flow.   A few years later he[10] recorded a dyke, containing basic inclusions and garnets, a mile further south.   In 1901 Card[6] described one of the Murrumburrah rocks as a monchiquite and gave an analysis of the rock together with two new analyses of the Byrock and El Capitan types.   Later the El Capitan rock was figured by Harker[14] in his " Petrology for Students ".

In 1915 the Geological Survey of N. S. Wales recorded leucite-bearing rocks from Lake Cudgellico and the Condobolin district, and one of these was analysed by W. A. Greig.[13]

Recently a specimen of a leucite-bearing basaltic rock was obtained from a well sunk through granite by Mr. Stevenson of Griffith. This rock was forwarded to the Mining Museum, and the Curator, Mr. H. F. Whitworth, has kindly allowed us to examine it.

In the present paper it is proposed to give further details of the Murrumburrah occurrence and to review other occurrences.

II. FIELD OCCURRENCE.

Murrumburrah is situated about one mile from Harden on the Main Southern Railway Line at a distance of 240 miles from Sydney. The leucite-bearing rocks occur in an arborescent dyke-like mass cutting granite in Portion 522, Parish of Murrumboola. Several small quarries expose the intrusion and reveal its complicated nature. In most cases the basic magma has made its way along joint planes in the granite, and when following horizontal joints it occurs as tabular sheet-like masses which are sometimes exposed at the surface and resemble a flow. It is probable that the intrusion occurred fairly close to the surface, and but little of its cover has been removed by erosion. Frequently off-shoots from the main intrusion completely surround and cut off blocks of granite, which, though retaining its original texture, becomes very dark in colour. It will be shown that the basic liquid has permeated and reacted with the solid granite of the included blocks. The granite at the contact of the intrusion is hardened but not otherwise altered.

The dyke reported by Curran[10] to contain garnets has not been examined, but the main mass examined by us contains inclusions of ultrabasic rocks as well as large idiomorphic or partly corroded crystals of pyroxene and biotite. These often measure two inches across, and one book of mica measuring four inches has been observed. Numerous cavities and veins filled with chlorite, carbonates, chalcedony and quartz are apparent in the field, and microscope examination has revealed an interesting suite of minerals occurring in this way.

We have not had an opportunity of examining the field occurrence of any of the other leucite-bearing rocks of N. S. Wales, but earlier reports leave little doubt that most of them occur as flows. The discovery of the Griffith rock in a shaft through granite suggests its intrusive nature.

III. PETROGRAPHY.

(i) The Murrumburrah Occurrence.

In view of the importance of late magmatic activity, it is proposed to describe the normal phase of the rock and to devote a special section to those parts that evidence this phenomenon. The ultrabasic inclusions and the hybridisation of the basic rock by granite will also be described separately.

(a) *Normal Phase.* In handspecimen these are fine-grained basaltic rocks with a sub-conchoidal fracture.

Under the microscope they are porphyritic and usually intersertal, but where the magma has cooled quickly in contact with the granite a very fine microcrystalline or cryptocrystalline groundmass has developed, the only mineral to have completely crystallised being magnetite, which occurs in small octahedra (Fig. 2B).

Biotite-bearing and biotite-free varieties are present and these may be subdivided into varieties with and without nepheline; rocks containing both biotite and nepheline are the most common types. Leucite is more abundant in the biotite-free types poor in nepheline and the analysis of such a rock appears in column II, Table I. In general the nepheline-rich varieties are slightly lighter in colour and coarser in grainsize.

Olivine is very abundant in all types and occurs as phenocrysts and microphenocrysts, which are idiomorphic to subidiomorphic and measure from $0 \cdot 75$ mm. to about $0 \cdot 2$ mm. The phenocrysts are often fresh, but the olivine, especially in the vicinity of the veins and cavities, is usually altered to either iddingsite or serpentine. The absence of iron ore inclusions from the pseudomorphs suggests that the original olivine was rich in the forsterite molecule, and this view is strengthened by the high magnesia in the analysed rocks.

Leucite usually occurs as small rounded micro-phenocrysts or as small irregular interstitial grains in the groundmass. In the larger crystals small radially arranged inclusions are conspicuous and alteration to analcite is not infrequent.

Idiomorphic crystals (up to $0 \cdot 7$ mm.) of pyroxene sometimes occur as micro-phenocrysts. These are zoned with an inner greyish-green core, followed by a zone of distinct purple colour and then by a greyish-purple margin. Augite, which is slightly titaniferous and of a greyish-purple

colour, is the most abundant mineral in the groundmass, where it occurs in a plexus of small ($\ll 0 \cdot 1$ mm.) prisms or rounded grains.

In the normal nepheline-bearing types nepheline occurs interstitially in the groundmass as poikilitic plates ($0 \cdot 7$ mm.). It is often accompanied or replaced by analcite (Fig. 1B). Sometimes, however, tiny idiomorphic crystals surrounded by a plexus of augite and magnetite are developed.

Biotite is a prominent mineral in most types and occurs as small (up to $0 \cdot 3$ mm.) poikilitic plates in the groundmass. X = straw yellow, Y = reddish brown, Z = dark reddish brown, $\alpha' = 1 \cdot 563$, $\gamma' = 1 \cdot 637$. In most cases the cleavage is rather poorly developed.

Magnetite is usually very abundant in the groundmass, where it occurs as perfect little octahedra. The analyses indicate very high titania in these rocks, and, although much of this is contained in the pyroxene, it is possible that the iron ore is a titaniferous magnetite.

No plagioclase has been detected with certainty in the groundmass of these rocks, although a few tests have been made by staining with malachite green. Card[6] was unable to recognise this mineral in the specimen examined by him, but in view of the analysis suggested that a small quantity might be present in the base. Although we do not deny this possibility, we consider that recent work on the composition of the pyroxenes[29] has shown that normative anorthite might easily be contained in the titanaugite which is so abundant in the Murrumburrah rocks.

(b) *Late Magmatic Phase.* Fine-grained types immediately adjacent to the granite contact as well as the slightly coarser normal types have been affected by end-stage processes, but in general the fine marginal types are the more susceptible. The late-stage minerals are usually deposited in small veins and cavities of a very sinuous nature and rarely measure more than 8 mm. In the vicinity of these cavities the olivine phenocrysts of the normal rock are altered to either iddingsite or serpentine but the former appears to be the more common. Sometimes the texture of the rock is a little coarser near the veins and in some of the rocks small coarser grained ocelli occur.

In the handspecimen these rocks have a characteristic hackly fracture, and, when rounded amygdules are present,

the fractured surface has a knotted appearance. The surface of one type shows small rounded knobs, the size of a pea, which are about an inch apart. Under the microscope it is seen that the nodules contain small ocelli about 1 mm. in diameter. These either consist of an aggregate of small rounded isotropic grains which appear to be leucite or show a border of idiomorphic leucite crystals with inwardly projecting radii of diopside and an infilling of chlorite. In other types small coarse granular ocelli consist mainly of diopside and a little chlorite.

The coarser areas adjacent to some of the veins differ widely in texture. One such patch shows an intergrowth of idiomorphic nepheline crystals (about 0·3 mm.), biotite, and titanaugite which suggests a graphic structure. The nepheline is associated with and partly altered to analcite. Alteration to zeolites and possibly to hydronepheline also occurs. Small stellate patches and tiny sheaves of titanaugite needles are embedded in some of the analcite, which has also been clouded with minute granules of iron ore and tiny needles of apatite. It is believed that the analcite containing pyroxene has replaced nepheline, as these two minerals are such constant associates. Several veins have been noted in which analcite borders carbonates and occurs as an interstitial mineral in the adjacent rock. The grainsize in the vicinity of such a vein is much coarser, and a texture differing from that of the normal rock is developed. Augite is richer in titania and a few millimetres away from the vein the crystals are more closely packed, giving the rock a pilotaxitic texture. Augite prisms are larger than usual and very variable in size, becoming larger in the area of analcite bordering the vein (Fig. 1D). The analcite often contains dendritic inclusions of a chlorite-like material which we have often observed in the nepheline of theralites, and which we believe to be identical with the " grid-like or herring-bone ribs with an interstitial background of poikilitic nepheline " observed by Holmes[17] (p. 95). Holmes suggests that this chloritic material may be chlorophæite. Although we have observed this material only in the analcite of the Murrumburrah rocks, there is evidence to show that it represents analcitised nepheline.

Large idiomorphic crystals of dark brown mica measuring from about ½ inch up to 4 inches in diameter are of common occurrence at Murrumburrah. In the handspecimen resorption is suggested by a rounding off of the crystal
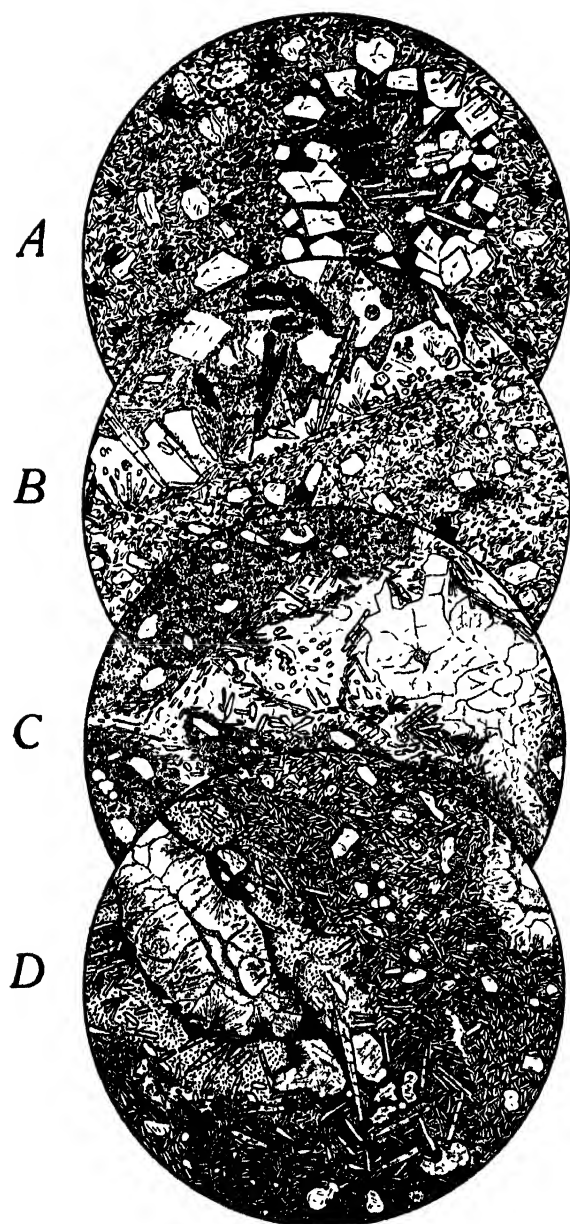
Fig. 1.   Late Magmatic Types, Murrumburrah.   ×14.

angles. It is difficult to prepare slides of this material and its origin has not been satisfactorily determined. In view of the fact that biotite arises as a late magmatic mineral (Fig. 1B), it is possible that this might be the origin also of the abnormally large crystals. The few rather poor microsections available show large optically continuous sections of biotite surrounded by and threaded with smaller flakes arranged in criss-cross fashion. Most of these appear to be separated from the normal rock by nepheline or other late magmatic minerals suggesting an end-stage origin for the biotite. These books of mica, however, represent such a large bulk of material that it seems possible that they may originally have been xenoliths of mica-peridotite or glimmerite which have become mobilised under the action of volatiles and have segregated with other late-magmatic minerals. Holmes has pointed out that biotite is a mineral which is very readily mobilised under pneumatolytic conditions.

Fig. 1. Late Magmatic Types, Murrumburrah. × 14.

A. Cavity in biotite-leucite-monchiquite. The cavity is lined with idiomorphic crystals of nepheline and the centre is infilled with blade-like crystals of titanaugite, dark chlorite clouded with inclusions of iron ore, a little biotite and carbonates. The enclosing monchiquite consists of phenocrysts of olivine mostly altered to iddingsite, in a groundmass of augite microlites with interstitial leucite deep brown biotite and little octahedra of iron ore.

B. Vein through nepheline-bearing leucite monchiquite. A large plate of interstitial nepheline may be seen on the left-hand side of the figure and a plate of analcite is present on the right. The vein is bordered by idiomorphic crystals of nepheline and blade-like or columnar crystals of titanaugite and biotite. The centre is filled with dark chlorite clouded with iron ores, as well as colourless plates of chlorite and skeletal crystals of biotite.

C. Part of a sinuous cavity lined with allotriomorphic grains of nepheline and small acicular crystals of titanaugite. Towards the centre of the cavity hedenbergite is developed instead of titanaugite, and the centre is infilled with carbonates.

D. End of a vein in pegmatitic type. The vein consists of carbonates with irregular grains of calcite mantled with fibrous aragonite. Bunches of carbonate needles (possibly aragonite) are growing into the calcite. The vein is bordered by dark chlorite, which passes out into analcite with dendritic inclusions of (?) chlorophæite. In the immediate vicinity of the vein analcite is interstitial, but at a distance of about one mm. the texture of the rock becomes pilotaxitic. Prisms of titanaugite are very variable in size and larger near the vein. A cavity lined with carbonates is shown in the N.E. quadrant.

Many of the veins and cavities are bordered with idiomorphic crystals of nepheline in close association with acicular crystals of reddish-brown biotite and pyroxene (see Fig. 1A, B, C). When more than one variety of pyroxene is present titanaugite is deposited before hedenbergite. Diopside, though common, does not appear to occur in cavities with titanaugite, but it is sometimes followed by the variety richer in iron.

The centres of these veins and cavities are infilled with carbonates and/or chlorite, the latter often crowded with minute needles of apatite and tiny grains of iron ore. When both carbonates and chlorite are present the deposition of the carbonate usually precedes that of the chlorite. Calcite is often " dog-tooth " but may occur as irregular grains. Bunches of minute carbonate filaments often appear to be growing from the wall of the cavity into the calcite grain (Fig. 1D). These have not been identified, but it is possible that they may be aragonite. A narrow mantle of fibrous aragonite also appears on the botryoidal surface of the calcite (Fig. 1D).

Yellow stilbite ($\alpha = 1 \cdot 494$, $\gamma = 1 \cdot 500$) may occur in sheaf-like bundles of radiating crystals on the surface of the calcite.

Chlorite may be colourless, pale green or brownish-green. The refractive index is usually lower than that of Canada balsam. Sometimes a fibrous radiating structure is developed, but the mineral usually occurs in large isotropic flakes.

(c) *The Granite Hybrids.* At the immediate contact with the granite the basic rock is chilled and the only recognisable minerals are microphenocrysts of altered olivine and minute grains of magnetite. The large included blocks of granite assume a dark colour, and on microscopic examination it is seen that its minerals are fractured and threaded with magnetite. Felspars are heavily sericitised, quartz strained and fractured, and biotite almost completely pseudomorphed by magnetite. A reddish-brown mineral with high refraction and birefringence occurs sometimes in little rounded grains. This is possibly fayalite.

A little closer to the basic rock, where tongues of the magma have penetrated the solid granite, biotite is entirely replaced by magnetite and may contain small inclusions of olivine; quartz is surrounded by minute granules of pyroxene which are separated from the comparatively

fresh felspar by veinlets of chlorite. Around the biotite there is a narrow rim of very fine trachytic material consisting of tiny microlites of orthoclase, flakes of chlorite, and minute iron ores (Fig. 2A). Incipient red-brown mica occurs in patches in the chlorite. In the handspecimen this rock, with its numerous xenocrysts, resembles a granite in texture, if not in colour, and might be referred to as the granite-hybrid.

Adjacent to the margin of the basic rock the basic hybrid is developed. This also consists of small, though slightly larger, laths of orthoclase in which have been embedded numerous xenocrysts of quartz, felspar and pseudomorphed biotite crystals that have been rifted off from the granite. This rock has an intersertal texture, the dark material between the orthoclase laths being chlorite and pyroxene (Fig. 2B). A little plagioclase is possibly present in this plexus, but none has been positively identified. Xenocrysts of microperthite show a fringe of tiny orthoclase laths in optical continuity with the xenocryst. Plagioclase xenocrysts are usually mantled with a narrow border of orthoclase and remnants of corroded quartz show trails of gas bubbles and a dark border which can be resolved under high power into granular augite, dark chlorite, and iron ore. Holmes observed gas bubbles and coronas of granular augite around the quartz xenoliths in many of the Uganda lavas.

Some of the granite fragments have travelled some distance into the basic magma and have been enclosed as xenocrysts (Fig. 2C). Quartz crystals are much corroded and shattered around the edge, where optically continuous fragments are threaded and surrounded by pale chlorite. The xenocryst appears to have been surrounded first by the titaniferous augite with which the magma was saturated. Prisms of diopside have grown inwards into the shatter zone from this barrier of titanaugite, and these are followed by a growth of hedenbergite which appears to be penetrating the shatter zone from the direction of the corroded xenocryst as well.

(d) *Ultrabasic Inclusions.* Fragments of dunite and chromite-bearing harzburgite, and elliptical inclusions of pyroxene are of common occurrence in the basic rock. The xenoliths measure up to about $\frac{3}{4}$ inch in diameter and the pyroxene xenocrysts are often more than an inch in diameter. As pointed out above (p. 425), the large crystals of biotite which are associated with end-stage

minerals possibly represent mobilized ultrabasic xenoliths consisting mainly of mica such as glimmerites, but as yet no such inclusion has been identified.

The harzburgite is a coarse-grained rock showing octahedral sections (0·6 mm.) of deep brown chromite associated with olivine and enstatite. Fresh olivine embedded in serpentine is very well developed, and
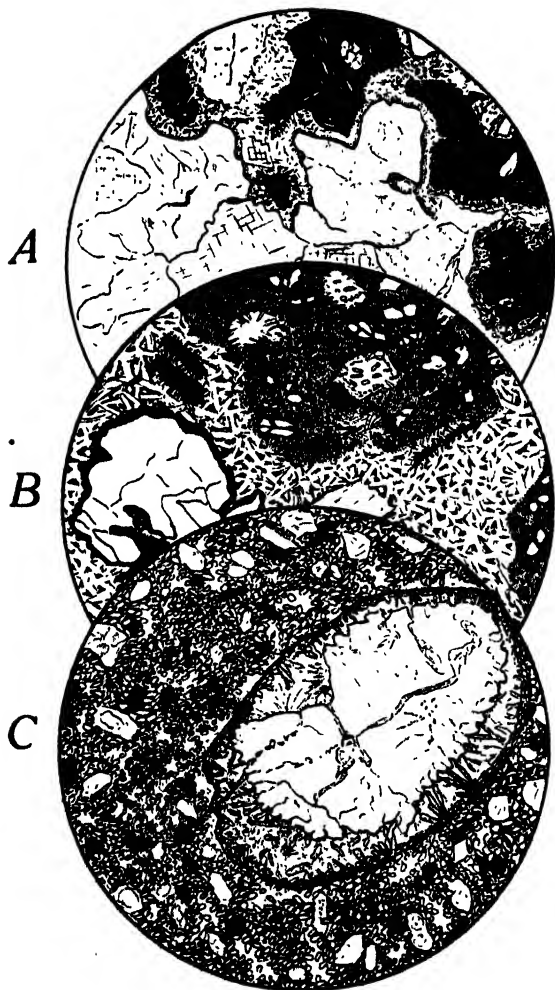
Fig. 2.   Monchiquite-granite Hybrids, Murrumburrah.   ×14.

irregular grains of enstatite are always surrounded by a kelyphitic border (Fig. 3A). A little carbonate material is also present.

Occasional xenocrysts of chromite and large skeletons of olivine occur in the basic rock, and it is believed that these represent almost completely disrupted and assimilated xenoliths of harzburgite.

The pyroxene xenoliths were possibly derived from pyroxenites, though no crystal aggregates have been detected. The xenocrysts are usually elliptical and partly resorbed. Under the microscope they appear to have recrystallised and possibly represent the break down of a complex pyroxene into simpler molecules. The centre zones usually have a very small optical axial angle and may be pigeonite. Iron ores have separated along definite crystallographic directions, producing a feather-like pattern. The outer zone of the xenocrysts is titanaugite, which shows no evidence of recrystallisation and appears to be a mantle of later origin (Fig. 3B). The smaller of these recrystallised elliptical pyroxenes are rather reminiscent of the zoned pyroxene-felspar bodies occurring in some of the Hartley gabbros.[19]

The partial analysis of a large pyroxene crystal from Murrumburrah has been quoted by Curran.[10] It is obvious that much of the iron estimated as the sesquioxide is present in the mineral as the monoxide, and the analysed material possibly represents a mixture of pyroxenes, as there are variations of composition within a single crystal. The analysis is useful, however, in giving an approximate

Fig. 2. Monchiquite-granite Hybrids, Murrumburrah.   × 14.

A. The lower part of the figure represents the normal granite, consisting of quartz and felspar. The upper part is the granite-hybrid, showing biotite crystals pseudomorphed by iron ore and surrounded by a " trachytic " border. A few olivine inclusions are present in the biotite pseudomorphs. Corroded grains of quartz are surrounded by a fine-grained corona of augite.

B. Sharp contact of fine-grained basic rock against hybrid-type which consists of a plexus of small orthoclase laths, granules of augite and dark chlorite with large xenocrysts of quartz and felspar. The corroded quartz xenocryst is surrounded by a dark border of granular augite, iron ore, and chlorite.

C. Leucite-bearing biotite monchiquite with xenocryst of quartz. The xenocryst is bordered with granular titanaugite and surrounded by a rim of fractured quartz grains and chlorite into which diopside and hedenbergite prisms have grown out from the titanaugite " barrier " and from the edge of the xenocryst.
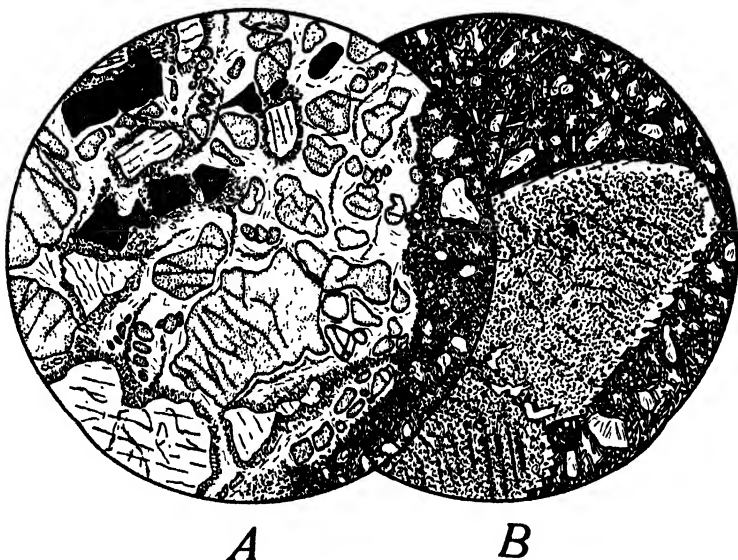
Fig. 3.   Ultrabasic Inclusions, Murrumburrah.   ×14.

A. Xenolith of chromite-bearing harzburgite consisting of olivine,
   enstatite, serpentine and chromite. The enstatite is surrounded
   by a kelyphitic border.

B. Xenocryst of pyroxene in a biotite-free leucite-bearing monchiquite.
   The xenocryst is roughly elliptical and shows recrystallisation with
   the separation of iron ores, and is mantled with fresh titanaugite.

idea of the composition of the original mineral, and it is
obvious that alumina entered the silica tetrahedron.[29]

(ii) Other Occurrences in New South Wales.

The leucite-bearing rocks from Byrock and from El
Capitan, about 50 miles to the south of Byrock, have been
described in some detail by other authors, [20, 8, 11] and it
is proposed to give only a brief summary here.   So far as
we are aware the rocks from about the Condobolin centre
have not been described, though reference has been made
to them by Browne[5] and a rock from Lake Cudgellico
has been analysed.[13]   The Griffith occurrence has not
yet been described and it is found that this rock bears a
remarkable resemblance to certain types from the other
two areas ; it is proposed to describe these rocks briefly,
not under the headings of their respective localities, but as
types that have common characters and which may occur
in all three localities.   Three distinct rock-types have
been recognised—one in which poikilitic plates of phlogopite

are developed, another in which nepheline is present in the groundmass, and a third with a microcrystalline ground-mass, which may represent a chilled marginal phase of either of the other two.   All contain some variety of mica.

(a) *Type with Poikilitic Phlogopite.*   Rocks of this type occur at El Capitan (Fig. 4A), 45 miles S.W. of Condobolin (Fig. 4D) and at Griffith, so it is a widespread type and compares chemically, mineralogically, and structurally with a rock from East Borneo described as a micaleucite basalt by Brouwer[4] (see Fig. 2).

These rocks are rich in olivine, which occurs always as phenocrysts or microphenocrysts in a groundmass of leucite, diopside microlites, iron ore, and large poikilitic plates of bright orange-yellow mica.

The grainsize of the rock from El Capitan, Ungarie, and Griffith varies a little.   At El Capitan the phenocrysts are smaller than elsewhere, measuring only about 0·3 mm., and the poikilitic micas measure only about 0·75 mm., but the groundmass is coarser than that of rocks from either of the other localities.   Here also the olivine is altered into limonite and carbonates, which seems to suggest that it was a variety richer in iron.   In the example 25 miles from Ungarie olivine phenocrysts average about 1·5 mm., and, although most of the mica occurs in rounded plates of about 1·5 mm. in diameter, large elongated flakes may attain a size of 3 mm. (see Fig. 4D).   In all these rocks the poikilitic mica is crowded with little rounded crystals of leucite, diopside microlites, and tiny grains of magnetite ; the mica is sometimes twinned.   In the Griffith specimen the following determinations have been made : $\alpha' = 1 \cdot 555$, $\gamma' = 1 \cdot 639$, $Z =$ light reddish brown, $Y =$ deep orange-yellow, $X =$ pale yellow, and this appears identical with the mineral occurring in the rocks from the other areas. Judd[20] remarked on the occurrence of bright yellow mica in rocks from the Byrock district in 1887, and it has since been mentioned by other authors.[11]   Although the optical properties are not identical with those of the titaniferous phlogopite described by Prider,[24] they are certainly closer to this than to normal phlogopite, and the high titania in the analysed rocks suggests a titaniferous variety.

The rocks at Griffith and at El Capitan contain ocelli and cavities indicating the action of late magmatic solutions.   The ocelli consist of leucite, diopside, and mica, or of small coarse patches of diopside or leucite
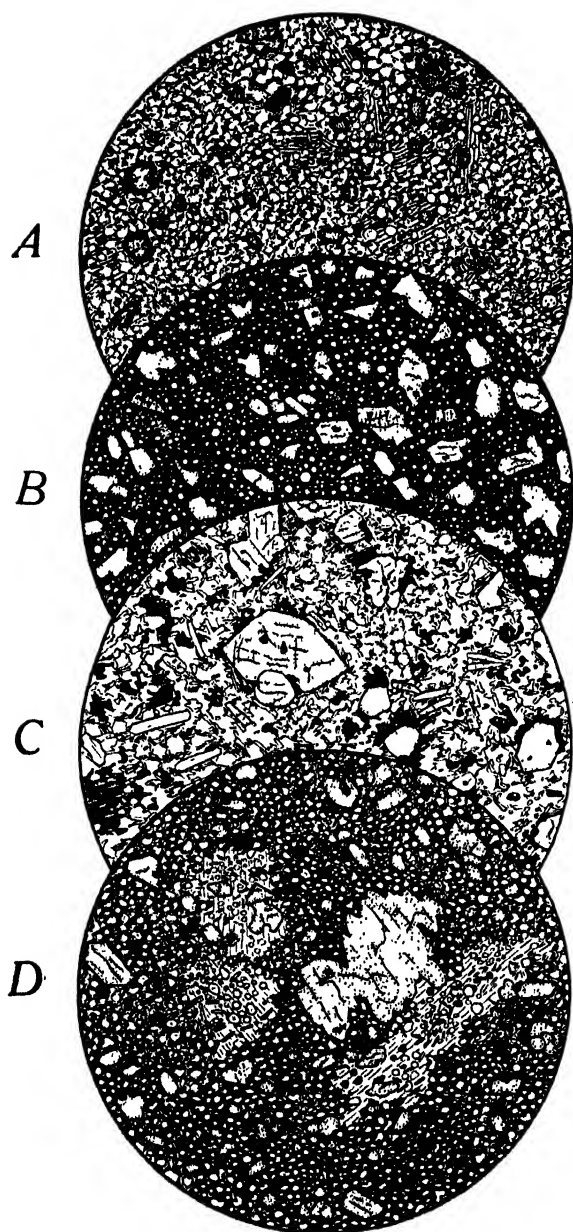
Fig. 4.   Mica-leucite Basalts from N. S. Wales.   ×14.

alone. In the Griffith rock cavities are filled with chlorite and analcite. Occasional xenocrysts, which were possibly felspar, have been completely analcitised and chloritised, and leucite crystals have grown into them from the groundmass. In the El Capitan rock a cavity containing a peculiar amphibole is present. Only a few sections of the amphibole occur, and the largest extinction angle measured is 14°, but this probably does not represent a maximum. X=pinkish fawn, Y=chocolate, Z=light chocolate brown ; Y>Z>X. The elongation is positive and the mineral optically negative. It occurs on the outer edge of the cavity in association with leucite, diopside, and mica, and the cavity is infilled with analcite with a core of chalcedony.

(b) *Nepheline-bearing Types.* All the specimens of this type have been collected from the Condobolin or Lake Cudgellico area, and reference to the normative composition shows the higher nepheline in these rocks.[5]

They are all very rich in olivine, which occurs as well formed phenocrysts. It has a positive character indicating a high magnesia content. Sometimes the olivine phenocrysts show glomeroporphyritic grouping and occasionally two crystals show a cruciform intergrowth. In addition to phenocrysts of olivine the rocks may sometimes contain smaller columnar phenocrysts of diopside (Fig. 4c), and a slight parallelism of these suggests a fluidal fabric.

The groundmass of these rocks consists of leucite, nepheline, diopside, iron ore, and small flakes of reddish-brown mica similar to that which occurs in the Murrum-

Fig. 4. Mica-leucite Basalts from N. S. Wales. ×14.

A. Microphenocrysts of olivine partly altered to limonite and iddingsite occur in a groundmass of leucite, diopside microlites, magnetite, and large poikilitic plates of phlogopite. El Capitan, 50 miles south of Byrock.

B. Phenocrysts of olivine and tiny microphenocrysts of leucite occur in a microcrystalline groundmass of augite and iron ore. A few small patches of biotite are also present in the groundmass. Bygalorie, about 45 miles S.W. of Condobolin. Compare fine-grained type from El Capitan figured by Harker.[14]

C. Phenocrysts of olivine and columnar crystals of diopside occur in a coarse groundmass consisting of leucite, diopside, nepheline, biotite, and iron ore. Lake Cudgellico, 50 miles S.W. of Condobolin.

D. Phenocrysts of olivine are present in a groundmass of leucite, diopside microlites, magnetite, and large poikilitic plates of phlogopite. Near Bygalorie, 45 miles S.W. of Condobolin and 25 miles N.W. of Ungarie.

burrah rocks. The larger of the mica plates are more yellowish in colour and have a tendency to poikilitic development. Though iron ore usually occurs in small octahedra, larger skeletal crystals are sometimes developed, and these suggest ilmenite.

One type from Lake Cudgellico is coarser grained than usual (Fig. 4c), and in this the leucite crystals are seen to contain numerous regularly arranged small round inclusions.

(c) *Types with Microcrystalline Groundmass.* An example of this type occurs at Bygalorie to the east of Lake Cudgellico, and Harker[14] has figured a similar rock from El Capitan. These possibly represent marginal phases of the other types.

Phenocrysts of olivine are well developed, and the groundmass consists of small rounded crystals of leucite surrounded by dark material which under the high power may be resolved into magnetite and tiny needles of pyroxene. There is an incipient development of dark reddish brown mica, which occasionally forms distinct small plates (Fig. 4b).

IV. PETROGENESIS.

(i) Pegmatitoid and Hydrothermal Stages.

Reference to the section dealing with the late-magmatic types indicates that both high and low temperature assemblages are developed and that these are closely associated in the same cavity or vein. Although the minerals in the following list are not all present in a single specimen, the examination of a number points to a very definite order of succession. Infillings of quartz and chalcedony were often noted in the field, and it was found that these were usually surrounded by soft material and readily weathered out. Unfortunately we appear to have overlooked the collection of this material, and none of the rocks sectioned contains either of these minerals. The field occurrence, however, suggests that they were the last minerals to crystallise at Murrumburrah, and a single cavity containing chalcedony in a rock from El Capitan indicates that it was later than analcite.

Leucite   ⎫
Nepheline   ⎪
Biotite, titanaugite or diopside and ⎬ Pegmatitoid Phase.
   amphibole at El Capitan   ⎪
Hedenbergite   ⎭

Analcite ⎫
Natrolite or hydronepheline (altera- ⎪
  tion product of nepheline) ⎪
Calcite ⎬ Hydrothermal or
Aragonite, stilbite ⎪   Deuteric Phase.
Chlorite ⎪
(?) Chalcedony and quartz ⎭

The first group of minerals, although they occur in vesicles, were deposited at high temperatures, possibly by sublimation. It is of interest to note that leucite has been recorded in the cavities of the Vesuvius lavas, and that nepheline and augite occur in the vesicles of the Capo di Bove nepheline-leucitites. Nepheline occurring in this way has also been recorded in the melilite-basalts of Hawaii[12] and the occurrence of biotite in cavities has been noted in the Eifel tephrites and described and figured by Holmes[17] from the vesicles of the Bufumbira lavas.

The term " pegmatitoid phase " was first introduced by Lacroix[21] to describe those coarse-grained patches and veins of high temperature minerals that other authors[18, 22, 26] have variously described as segregations and schlieren. Dunham[12] has employed the term in describing the occurrence of nepheline and associated minerals in the cavities of the Hawaiian lavas.

At Murrumburrah, as at Honolulu and Prospect, the higher temperature or pegmatitoid stage is followed by the lower temperature hydrothermal or deuteric stage, when water and carbon dioxide were the active agents of deposition. Owing to its small size and probable shallow burial, the Murrumburrah intrusion cooled rapidly and end-stage processes were thus restricted, but it is significant that these late-magmatic types are more abundantly developed near the chilled margin which was rapidly cooling, contracting, and cracking, and where magmatic fluids were finding a means of escape. Had these been trapped in the main body of the rock it is probable that coarser grained and more profoundly altered types would have resulted.

(ii) Hybridization by the Granite.

A limited amount of hybridisation of the basic rock has taken place at its contact with the granite, but owing to the rapid cooling modification has been but slight.

The unaltered granite consists of quartz, microperthite, biotite, plagioclase, muscovite, and minor accessories. In the field the margin of the basic rock is sharp against a

dark coloured modified granite. Under the microscope a fine-grained basic rock shows a sharp contact with a hybrid rock which gradually merges into the granite. The hybrid penetrates the granite in minute tongues.

It is obvious that large quantities of iron oxide have been released from the basic magma and this material has completely replaced the biotite of the granite, setting free alumina, potash, and magnesia, which no doubt are precipitated as orthoclase and chlorite in the narrow trachytic rim surrounding the biotite pseudomorphs (see Fig. 2A). Some of the magnesia, together with iron, may form occasional crystals of olivine.

Coronas of diopsidic augite about quartz crystals point to reaction between the solid quartz and the lime and magnesia of the basic magma. The converse of this has been noted at the contact of dolomitic limestones where silica has been introduced from the magma.[27] Quartz xenocrysts surrounded by a corona of augite granules have been noted by Holmes,[17] who has also observed fusion of quartz and orthoclase and the deposition of the glass along cracks in the xenocrysts.[16] At Murrumburrah, however, neither mineral seems to have suffered transfusion, and, though isotropic material with a low refractive index occupies cracks, this is believed to be a form of chlorite. Dr. W. R. Browne has drawn our attention to a quartz xenocryst with a corona of pyroxene in the Prospect dolerite, and Benson[3] has figured a very similar structure from a basalt near Tamworth. In the latter case the siliceous material is opal, not quartz, and Benson regards the structure as a vesicle surrounded by pyroxene and infilled with opal, but it seems likely that an original xenocryst may have been altered by magmatic waters (see p. 433).

At Murrumburrah the felspars of the granite are fractured but show evidence of marked chemical stability. Corona structures are absent, and outgrowths of tiny orthoclase laths, which are optically continuous with original crystals of microperthite, indicate that this latter mineral was in equilibrium with the hybridised liquid.

Granules of augite occur in the slightly coarser grained hybrid adjacent to the margin of the chilled basic rock, and this type might be regarded as the modified monchiquite. Both hybrids, therefore, differ from the basic rock in their greater acidity and in their felspar content. Orthoclase is developed instead of leucite, and augite arises in place of

the ubiquitous olivine of the normal types.   Quartz is not in equilibrium in either hybrid, and where xenocrysts of this mineral occur they are separated from the hybrid rock by coronas of pyroxene.

(iii) Ultrabasic Xenoliths and their Possible Significance.

In discussing the origin of leucite-bearing magmas, Holmes[17] has laid stress on the frequent occurrence of ultrabasic xenoliths, particularly of mica-peridotite. Although we have not identified any mica-peridotites at Murrumburrah, other ultrabasic inclusions are abundant and their scattering and partial resorption suggests that a good deal more of this basic material may have been present originally, and that it has been assimilated by the monchiquite magma. Ultrabasic inclusions have also been noted in monchiquite dykes at Bulli,[15] Gerringong.[2] and Kiama,[25] and they are numerous in some of the volcanic necks of the Sydney district,[1, 23] where they are associated with somewhat sodic basalts.

We have not visited any occurrence of leucite-rocks in N. S. Wales except that of Murrumburrah, but there appears to be no record of such inclusion occurring in them, so we do not feel competent to discuss their origin in the light of Holmes' or any other theory. Moreover, the note on the Murrumburrah occurrence is by no means an exhaustive petrological study, and we feel that it would be unwise to base any conclusions upon our observations there.

The scattered occurrence of leucite-bearing rocks in N. S. Wales was emphasised by Browne,[5] who shows, with the aid of a map, that small outcrops up to fifty miles apart may be grouped into areas which are separated by many hundreds of miles. These rocks cut or overlie granites and Palæozoic rocks, but it is believed that they are all of Tertiary age. Their scattered development points to a unique set of conditions under which they have originated, and their genesis cannot be traced until the origin of the other Tertiary lavas, many of them containing ultrabasic inclusions, has been worked out.

V. NOMENCLATURE.

Curran[8] first described the Murrumburrah rock as a leucite basalt, and later Card redescribed it as a leucite monchiquite.[6] Comparison of the four analyses of this rock (Table I, columns I, II, III and IV) with the average

TABLE I.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
SiO$_2$ ..	39·51	40·10	40 25	41·72	41·14	40·95	43·58	44·50	44·74
Al$_2$O$_3$ ..	15·05	13·59	10 83	13·55	12·67	15·37	11·46	11·67	11·82
Fe$_2$O$_3$ ..	2·43	4·27	5·30	2·54	4·72	6·36	3·40	2·05	3·89
FeO ..	9·22	8·11	8·00	8·87	7·25	4·38	9·13	8·90	7·06
MgO ..	12·39	12·03	12 53	11·56	11·30	10·46	10·80	13·25	14·28
CaO ..	10·96	10·12	9·64	9·88	12·02	11·67	9·88	10·18	9·61
Na$_2$O ..	4·50	3·93	3·76	3·24	2·80	3·97	2·18	2·53	2·16
K$_2$O ..	1·67	1·28	1·48	1·51	1·27	1·26	2·13	2·91	2·51
H$_2$O + ..	2·13	2·71	2 58	2·01	2·60	3·93	2·40	0·44	0·40
H$_2$O − ..	0·24	0·85	0·78	0·39	0·74	0·86	0·47	0·12	0·10
TiO$_2$ ..	2·19	2·32	2·74	2·26	3·46	0·25	3·32	2·55	2·10
P$_2$O$_5$ ..	nd.	0·91	0·73	1·09	—	0·09	0·95	0·62	0 66
MnO ..	0·10	0·13	0·30	0·13	—	tr.	tr.	0·16	0·19
CO$_2$ ..	abs.	abs.	1·14	1·53	0·08	—	tr.	0·05	0 21
etc. ..	—	—	0·32	—	—	0·29	—	0·50	0·28
	100·39	99 85	100 38	100·28	100·05	99·84	99·70	100·43	100·01
Less O ..	—	—	—	—	—	—	—	0·03	0 05
								100 40	99 96
Sp. Gr. ..	3·04	3·04	3·024	3 03	—	2 932	—	3 06	—

I. Monchiquite. Por. 522, Parish of Murrumboola, Murrumburrah. Anal. Madeleine H. Harvey.

II. Biotite-free Monchiquite, Par. 522, Par. of Murrumboola, Murrumburrah. Anal. Madeleine H. Harvey.

III. Monchiquite, Murrumburrah. Anal. H. P. White. *Rec. Geol. Surv. N.S.W.*, 7, p. 302.

IV. Biotite-rich Monchiquite. (Fine grained marginal type slightly altered by end-stage processes). Por. 522, Parish of Murrumboola, Murrumburrah. Anal. Madeleine H. Harvey.

V. Limburgite. Dark green variety from part of Limburgite-Flow No. II, Kaiserstuhl, Baden. Anal. G. Stecher. W. Meigen and G. Stecher, *Mitt. Grossh. Geol. Badischen Landesanst.*, 8 (1), 1915, p. 170.

VI. Limburgite. Cerro Tacumbu, Paraguay. Anal. A. Lindner. L. Milch. *T.M.P.M.*, xxiv, 1905, p. 214. In W.T. No. 1, p. 693.

VII. Limburgite. No. 4 Quarry, Woodend, Macedon District, Victoria. Anal. R. J. Lewis. E. W. Skeats and H. S. Summers, *Geol. Surv. Victoria*, Bull. 24, 1912, p. 28.

VIII. Ugandite. C. 2809, Muganza. Anal. H. F. Harwood. A. Holmes and H. F. Harwood, The Volcanic Area of Bufumbira. *Geol. Surv. Uganda*, Mem. No. III, 1936.

IX. Murambite. Kanemagufa Valley, South of Mikeno. Anal. Research Dept. Messrs. Imperial Chemical Industries (Fertiliser and Synthetic Products) Ltd., Billingham, Co. Durham. A. Holmes and H. F. Harwood, "The Volcanic Area of Bufumbira," *Geol. Surv. Uganda*, Mem. No. III, 1936.

composition of twelve leucite-basalts (Table II, column IX) shows marked chemical differences. Reference to Table I will show that these rocks compare most closely with certain limburgites and in the absence of glass it seems best to retain Card's name of leucite-monchiquite.

An attempt has been made to use Holmes' classification[17] of the leucite-bearing rocks, and in columns VIII and IX (Table I) two analyses of the African rocks are quoted. It will be seen that the main difference between them and the Murrumburrah rocks lies in the alkalis. In the African examples soda and potash are approximately equal,

TABLE II.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
SiO$_2$	43 58	44·68	45·18	42 65	46 04	45·82	46·06	41·71	46·18	46 90
Al$_2$O$_3$	8·08	11·43	9·31	9 14	12·40	6 86	10·01	8·55	12·74	16·33
Fe$_2$O$_3$	5 00	7·00	6 31	5·13	3·54	6 07	3 17	2 51	5·27	4·22
FeO..	5·77	4·67	4·08	1·07	5 58	1·98	5·61	9·79	5 06	4·14
MgO	12·91	10 25	10·77	10·89	12·60	10·90	14 74	14·65	8·36	5·03
CaO	8·88	9·44	8·56	12·36	8·38	4·70	10·55	11 74	8 16	9·72
Na$_2$O	0·90	1·56	1·73	0 90	1·62	0·84	1·31	0·60	2·36	2·75
K$_2$O	5·99	5·68	6·93	7·99	4 87	8·82	5·14	3 65	6·18	7·58
H$_2$O +	1·95	2·73	1 01	2 18	}3 55	0 75	1 44	1·41	}2·60	}1·50
H$_2$O −	1·15	0·77	0·55	2·04		2·40	—	0·16		
TiO$_2$	4·64	0·84	4·36	1·64	2·20	7 34	0·73	2·15	2·13	1·22
P$_2$O$_5$	0·62	0·66	0·51	1·52		1·83	0·21	1·62	0·77	0·50
MnO	0·21	0·11	tr.	0·12		0 10	tr.	0·24	0·19	0·11
CO$_2$	0·11	0·20	0·17	—		0 08	—	0·16		
BaO	0·32	0 02	0·30	0 89		1 27	0·32	0 50		
etc.	0 14	0·15	0 10	1·59		0 17	0·28	0·38		
	100·25	100 19	99·87	100·11	100·78	99 93	99·57	99·82	100·00	100·00
Loss O	—	0 02	0·01	0·01						
		100·17	99 86							
Sp. Gr.	2 897	2 944	2·980	2·857						

I.   Leucite Basalt. El Capitan. Anal. H. P. White. *Rec. Geol. Surv. N.S.W.*, 7, p. 302.
II.   Leucite Basalt. Lake Cudgellico. Anal. W. A. Greig. *Ann. Rept. Dept. Mines N.S.W.*, 1915, p. 196.
III.   Leucite Basalt. Byrock. Anal. J. C. H. Mingaye. *Rec. Geol. Surv. N.S.W.*, 7, p. 302.
IV.   Madupite. Pilot Butte, Leucite Hills, Wyoming. Anal. W. F. Hillebrand, W. Cross. *Amer. Journ. Sci.*, 1897, 4, 130.
V.   Mica-leucite-basalt. Oeloe Kajan, East Borneo. Anal. A. Pisani, H. A. Brouwer *Pr. K. Ak. Wet. Amst.*, (1), 1909, 12, p. 151.
VI.   Wolgidite (No. 456A, Mt. North). Anal. C. R. Le Mesurier. A. Wade and R. T. Prider, *Quart. Journ. Geol. Soc.*, 1940, 96, p. 75.
VII.   Missourite. Shonkin Stock, Montana. Anal. E. B. Hurlbut. L. V. Pirsson, *U.S.G.S. Bull.* 237, 1905, p. 117.
VIII.   Biotite-pyroxenite. Newry Complex. Seeconnell, Co. Down, Northern Ireland. Anal. L. S. Theobald. Doris L. Reynolds, *Quart. Journ. Geol. Soc.*, 1934, 90, 608.
IX.   Average Composition of twelve leucite-basalts. R. A. Daly, *Igneous Rocks and the Depths of the Earth*, 1933, p. 24, No. 107.
X.   Average Composition of Nine Leucitites. R. A. Daly, *Igneous Rocks and the Depths of the Earth*, 1933, p. 24, No. 108.

with potash slightly higher than soda, and in the Australian rock soda greatly exceeds potash. The high soda is expressed mineralogically in the presence of nepheline and/or analcite, minerals which are absent from the African ugandites and murambites, though present in some of the other rocks from that region. There seems no reason why a nepheline-bearing ugandite should not occur, and if such a rock be discovered it should compare closely with the Murrumburrah monchiquite.

Plagioclase has not been detected in the Murrumburrah rock, and in this it differs from the murambite. This, however, appears to be a modal rather than a normative difference. Norms have been calculated for the Murrum-

burrah rocks, but as slight differences of composition
appear to be overemphasised, it is considered that a
comparison of the norms will serve no useful purpose.

The leucite-bearing rocks from the Byrock and Con-
dobolin districts have always been referred to as leucite-
basalts.   The three analyses of these rocks indicate great
uniformity in their chemical composition, and though the
Griffith type has not been analysed it appears to show
marked mineralogical and structural affinities to these
types.   If these analyses (Table II, columns I, II and III)
be compared with the average analysis of twelve leucite-
basalts (column X) it will be seen that there is a marked
difference in their chemical composition. In the N. S. Wales
examples the average ratio of K_2O/Na_2O is about $4\cdot5$,
whilst that of the average leucite-basalt is $2\cdot6$.   Again
magnesia, and often titania, is a good deal lower in the
typical leucite-basalts.   The higher magnesia and titania
in the N. S. Wales rocks finds mineralogical expression in
the presence of titaniferous phlogopite, which is a dis-
tinctive mineral in these rocks and is absent from the
leucite-basalts.   The   N. S. Wales   rocks   are,   therefore,
excluded from the leucite-basalt group on both chemical
and mineralogical grounds.

A fairly wide search has been made in the literature
dealing with leucite-bearing rocks, and it is found that
there are few occurrences that have developed from a
magma with a K_2O/Na_2O ratio comparable with that of
the N. S. Wales types.   The closest analysis is that of a
madupite,[7] though this rock contains higher lime and
potash, indicated by the development of phenocrysts of
diopside and phlogopite and the absence of olivine.
Mineralogically, therefore, the rocks are dissimilar.

The missourite differs chemically in containing higher
lime and magnesia and mineralogically in the absence of
mica.

In classifying the rocks of the Western Kimberleys
Wade and Prider[28] found that they were unusually rich
in potash and low in soda, and, though potash is not so
high in rocks from N. S. Wales, they show some affinities,
both   chemical   and   mineralogical,   with   the   wolgidite
described by Prider.

Though a little higher in silica and lower in potash, the
mica-leucite-basalt from East Borneo[4] appears to compare
most closely chemically, mineralogically, and structurally
with the N. S. Wales rocks.   It seems evident that the

magma giving rise to these types, though uniform over a large area in N. S. Wales, was of unusual composition ; but it is not desirable to give this rock-type a new name, at least not until a more exhaustive study has been carried out, and in the meanwhile we suggest that the rocks might be termed mica-leucite-basalts, or called by the more general name of lamproite, to several types of which they show resemblance (madupite, wolgidite, etc.).

VI. ACKNOWLEDGMENTS.

In conclusion we gratefully acknowledge the hospitality and kindness of Mr. and Mrs. A. M. Hall of Murrumburrah, and for their assistance in the field we are grateful to Miss Marjorie Hopwood, B.A., and Mr. L. R. Hall.

Finally, we wish to thank Dr. W. R. Browne for kind criticism and helpful suggestions, and Mr. H. F. Whitworth for the loan of microslides.

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SYNTHETIC EXPERIMENTS WITH 3- AND 4-AMINOQUINALDINES.

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and ERNEST RITCHIE, M.Sc.

Whilst it is relatively easy to start from an aromatic amine and to build a new fused heterocyclic ring containing the nitrogen atom on to the benzene ring, the synthesis of analogous substances from the amino pyridines is usually very difficult. Thus, the ready synthesis from aniline of heterocyclic substances of the indole and quinoline types is not paralleled in the aminopyridine series, cf. e.g. Gulland and Robinson (*J.C.S.*, 1925, *127*, 1493), and derivatives of the pyridine analogous of indole (the pyrrolo-pyridines) and quinoline (the naphthyridines) are not numerous. Any consideration of the properties of the aminopyridines, and comparison of them with aniline quickly shows that there are many important differences, especially between aniline on the one hand, and 2- and 4-amino pyridines on the other. 3-Aminopyridine resembles aniline somewhat more closely, and, for example, can be diazotised in the usual manner (Mohr, *Berichte*, 1898, *31*, 2495) ; and it also behaves as a diacidic base in contrast to 2- and 4-aminopyridines, which behave as monacidic bases.

The experiments described in the present paper were designed to study the application of some of the methods of heterocyclic ring synthesis, which go so easily with aniline, to 3- and 4-aminoquinaldines.

Attempts to condense 4-aminoquinaldine with ethyl acetoacetate in presence of a few drops of 1 : 1 hydrochloric acid (cf. Coffey, Thomson and Wilson, *J.C.S.*, 1936, 856) to the corresponding β-(4-quinaldylamino) crotonic ester, with the object of cyclising this by Limpach's method (*Berichte*, 1931, *64*, 969-70) were unsuccessful. Somewhat more success attended the formation of 4-acetoacet-amidoquinaldine (I) by reaction together of 4-amino-quinaldine and ethyl acetoacetate at 160°. This amide

could be cyclised with concentrated sulphuric acid to the naphthyridine derivative II.

I   II
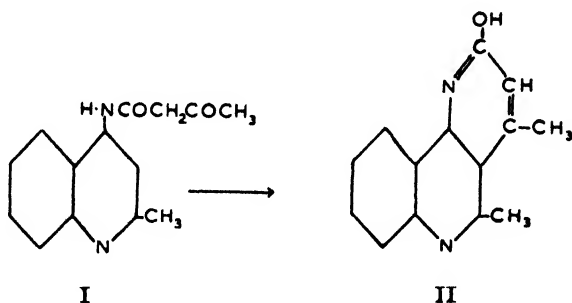
Marckwald (*Annalen*, 1894, *279*, 1) reported that the Skraup and Dobner-Miller quinoline syntheses can be applied successfully to 4-aminoquinaldine, and because he published no experimental details we have repeated and confirmed this work.   However, our attempts to carry out the Combes quinoline synthesis failed because 4-amino-quinaldine could not be condensed with acetylacetone. Attempts to condense 4-aminoquinaldine with acetonyl-acetone (cf. Hazlewood, Hughes and Lions, THIS JOURNAL, 1937, *71*, 92) to the 4-N-pyrryl-quinaldine derivative III were also abortive.

III   IV
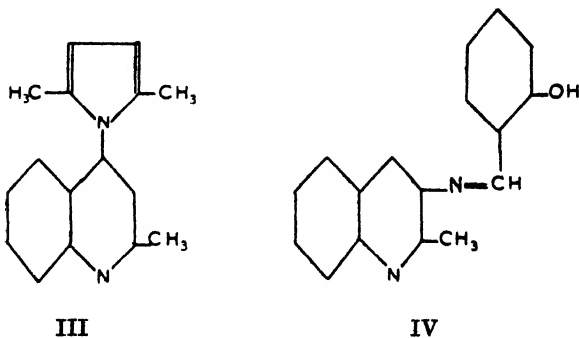
3-Aminoquinaldine (Perkin, Lawson and Robinson, *J.C.S.*, 1924, *125*, 635) was found to condense normally with salicylaldehyde to the salicylidene compound IV. Attempts to convert it into β-(3-quinaldylamino)-crotonic ester failed, although on one occasion success seemed to have been achieved. However, the conditions of this

unique experiment could not be reproduced. Prolonged heating of 3-aminoquinaldine with ethylacetoacetate at 100° or 20 minutes' heating at 160° led to formation of 3-acetoacetamido quinaldine, but this could not be cyclised to a naphthyridine derivative.

The relatively normal behaviour of the amino group of 3-aminoquinaldine was emphasised by its easy condensation with acetonlyacetone and phenacylacetoacetic ester to the pyrrole derivatives, V and VI ; and by its condensation with acetylacetone to the Schiff's base VII, which, however,
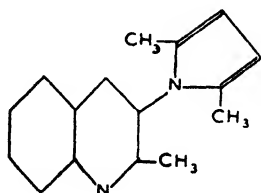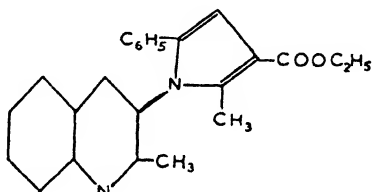
V   VI

could not be cyclised to a naphthyridine. The Skraup reaction was applied to 3-aminoquinaldine, but this also led only to the formation of tarry material and no isolable naphthyridine derivative.

Finally, it should be reported that application of Gabriel's " Glycine ester-Isoquinoline " synthesis (*Berichte*, 1900, *33*, 980 ; cf. also, Gabriel and Colman, *Berichte*, 1902, *35*, 1360 ; and Fels, *Berichte*, 1904, *37*, 2133) to the imide of quinaldine-3 : 4-dicarboxylic acid led to the formation of the 2 : 7-naphthyridine derivative VIII or IX, of which the former is probably the more likely (cf. Gabriel and Colman, *loc. cit.*).
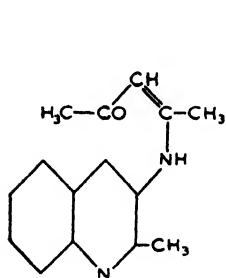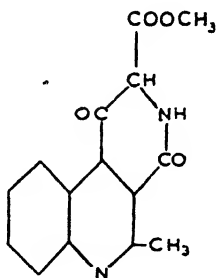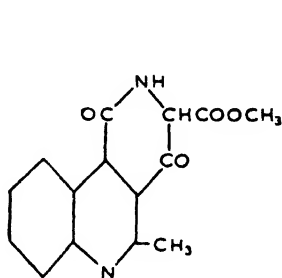
VII   VIII   IX

EXPERIMENTAL.

4-Aminoquinaldine. This base has been previously prepared by Ephraim (*Berichte*, 1893, *26*, 2228) by zinc and hydrochloric acid reduction of 4-(β-phenylhydrazino)-quinaldine ; and by H. Meyer (*Monats. für Chemie*, 1907, *28*, 52) by Hoffmann degradation of 2-methyl cinchonin amide. We prepared it by this latter method, and because the details of Meyer's method were not available the details of the method employed are briefly described. 2-Methyl cinchoninamide (D.R.P. 290, 703 ; Friedlander, *12*, 724 ; 17·5 g.) was added in one lot to a well-stirred ice-cold solution of potassium hypobromite (from bromine (15 g.) and potassium hydroxide solution (250 ml. of 10%)). After stirring for 45 minutes, the clear solution was treated with more potassium hydroxide (150 ml. of 10%) and stirred for a further 5 minutes at 0°. The reaction mixture was then heated to 80° for 20 minutes, when 4-aminoquinaldine (13·5 g.) crystallised out. After recrystallisation from benzene it melted at 164°.

4-Acetoacetamidoquinaldine (I). 4-Aminoquinaldine (4·8 g.) was added in one lot to ethylacetoacetate (20 g.) maintained at 160°. Effervescence occurred. After 15 minutes the mixture was cooled. The solid which separated was collected (3·5 g.) and recrystallised from much alcohol. It formed pale yellow needles which melted (with decomposition) at 256°. It is soluble in both dilute acids and alkalis.

Found : C = 69·7, H = 5·7, N = 11·8%. Calculated for $C_{14}H_{14}O_2N_2$, C = 69·0, H = 5·8, N = 11·6%.

2-Hydroxy-4 : 5-dimethyl-7 : 8-benzo-1 : 6-naphthyridine (II). The amide I (1 g.) was dissolved in ice-cold concentrated sulphuric acid (10 ml.) and the solution then finally heated at 100° for 10 minutes. After cooling, diluting and basifying with ammonia, the precipitated solid (0·6 g.) was collected and recrystallised from much alcohol, from which it separated in small pale yellow needles which darkened at about 280° and decomposed at about 290°.

Found : N = 12·5%. Calculated for $C_{14}H_{12}ON_2$, N = 12·5%.

5-Methyl-7 : 8-benzo-1 : 6-naphthyridine. The details of this preparation were as follows :

A mixture of 4-aminoquinaldine (20 g.), arsenic oxide (20 g.), glycerol (40 g.) and concentrated sulphuric acid (40 g.) was heated at 140-150° for 4 hours. The reaction mixture was then cooled, diluted to 500 ml. with water and made alkaline. The black, tarry precipitate which separated was collected and extracted with benzene (200 ml.). The extract was dried and the solvent removed, leaving a thick dark syrup which was distilled at atmospheric pressure without a thermometer. The distillate (1·2 g.) quickly solidified to a mass of yellow needles,

which were drained on a porous tile and then recrystallised from benzene, yielding clumps of small yellow needles melting at 206°.

Found : $N = 14 \cdot 2\%$. Calculated for $C_{13}H_{10}N_2$, $N = 14 \cdot 4\%$.

The picrate crystallised from alcohol in orange needles, which sintered at 230° and then melted at 245-246° (with decomposition).

Found : $N = 16 \cdot 5\%$. Calculated for $C_{19}H_{13}O_7N_5$, $N = 16 \cdot 6\%$.

Marckwald (loc. cit.) gives the melting point of the base as 206°, and of the picrate as 243°.

2 : 5-Dimethyl-7 : 8-benzo-1 : 6-naphthyridine. A mixture of 4-amino-quinaldine (16 g.), concentrated hydrochloric acid (60 ml.), anhydrous zinc chloride (5 g.) and paraldehyde (20 g.) was heated on the water-bath. A vigorous reaction occurred and the mixture became very dark. After 4 hours' heating the reaction mixture was diluted with hot water, filtered and basified. The precipitated tar was collected and extracted with boiling benzene (300 ml.) which deposited some 4-aminoquinaldine (7 g.) on cooling. The benzene mother liquor was evaporated to dryness and the residue distilled without a thermometer. The solidified distillate (0·7 g.) was fractionally crystallised from petroleum ether, small colourless needles (0·1 g.) melting at 95-96° being eventually separated from less soluble 4-aminoquinaldine.

Found : $N = 13 \cdot 6\%$. Calculated for $C_{14}H_{12}N_2$, $N = 13 \cdot 5\%$.

The picrate separated from alcohol in very sparingly soluble yellow needles melting at 225° (decomp.).

Found : $N = 16 \cdot 0\%$; calculated for $C_{20}H_{15}O_7N_5$, $N = 16 \cdot 0\%$.

Marckwald (l.c.) records the melting point of this base as 104°, and that of the picrate as 225°.

3-Salicylidene aminoquinaldine (IV). 3-Aminoquinaildine (1 g.) and salicylaldehyde (0·8 g.) were heated together at 100° for 30 minutes. On cooling and rubbing the product solidified. It was recrystallised from alcohol and thus obtained in yellow needles melting at 139°.

Found : $N = 10 \cdot 9\%$; calculated for $C_{17}H_{14}ON_2$, $N = 10 \cdot 7\%$.

3-Acetoacetamido quinaldine. 3-Aminoquinaldine (5 g.) was added in one lot to ethylacetoacetate (20 g.) maintained at 160°. Effervescence occurred. After 20 minutes the reaction mixture was cooled and the separated crystalline solid (4 g.) collected. Recrystallised from benzene it formed colourless needles melting at 149°.

Found : $N = 11 \cdot 8\%$; calculated for $C_{14}H_{14}O_2N_2$, $N = 11 \cdot 6\%$.

Attempts to cyclise this substance with concentrated sulphuric acid proved abortive. It could be recovered unchanged from a solution in concentrated sulphuric acid which had been kept at 0° for 24 hours ; whilst heating with concentrated sulphuric acid at 100° for 30 minutes caused complete hydrolysis.

N-(3'-quinaldyl)-2 : 5-dimethyl-pyrrole (V). A solution of acetonyl-acetone (2·3 g.), 3-aminoquinaldine (3·2 g.) and glacial acetic acid (1 ml.) in alcohol (15 ml.) was gently refluxed for 30 hours. Then,

after cooling, it was diluted with water and basified, and the precipitate collected. It proved to be easily soluble in the usual organic solvents, but was finally obtained in pale pink rhombs melting at 71° by allowing its solution in petroleum ether to evaporate at room temperature. Yield, 80%.

Found : $N = 12\%$; calculated for $C_{16}H_{16}N_2$, $N = 11 \cdot 9\%$.

The picrate separated from alcohol in deep yellow needles melting at 190°.

Found : $N = 15 \cdot 3\%$; calculated for $C_{22}H_{19}O_7N_5$, $N = 15 \cdot 1\%$.

N-(3'-quinaldyl)-2-phenyl-5-methyl-pyrrole-4-carboxylic ester (VI). A solution of 3-aminoquinaldine ($3 \cdot 2$ g.), phenacylacetoacetic ester (5 g.) and glacial acetic acid (1 g.) in alcohol (20 ml.) was refluxed for 70 hours. On cooling and scratching the product (6 g.) crystallised. Recrystallised from alcohol, it was obtained in colourless needles melting at 166°.

Found : $N = 7 \cdot 7\%$; calculated for $C_{24}H_{22}O_2N_2$, $N = 7 \cdot 6\%$.

β-*(3-Quinaldyl)-propenyl methyl ketone* (VII). A solution of acetylacetone (2 g.), 3-aminoquinaldine ($3 \cdot 2$ g.) and glacial acetic acid (1 g.) in alcohol (15 ml.) was refluxed for 80 hours, cooled, diluted, and extracted with ether. After drying, the ethereal extract was concentrated and allowed to stand, when the product (3 g.) crystallised in large pale yellow rhombs which melted at 96°.

Found : $N = 11 \cdot 9\%$; calculated for $C_{15}H_{16}ON_2$, $N = 11 \cdot 7\%$.

Attempts to cyclise this substance, using concentrated sulphuric acid, phosphorus oxychloride and phosphorus pentoxide in boiling toluene, all failed.

Ethyl 2-methyl-quinoline-3 : 4-dicarboxylimidoacetate. Preliminary experiments to prepare the potassium salt of quinaldine-3 : 4-dicarboxylic acid imide by treating an alcoholic solution of the imide with alcoholic potassium hydroxide were unsatisfactory because the potassium salt separated in a gelatinous mass which was very difficult to manipulate. Eventually, the following method was adopted : A solution of sodium ($1 \cdot 2$ g.) in absolute alcohol (30 ml.) was added to a solution of 2-methyl quinoline-3 : 4-dicarboxylic imide ($10 \cdot 6$ g.) in absolute alcohol (600 ml.), and the solution concentrated to 100 ml. Ethyl bromoacetate ($8 \cdot 4$ g.) was then added and the solution refluxed until it was neutral (about 3 hours). On cooling the nearly pure product (7 g.) crystallised out, and was collected, washed with warm water, and then recrystallised from alcohol, from which it separates as pale yellow needles melting at 159°.

Found : $N = 9 \cdot 5\%$; calculated for $C_{16}H_{14}O_4N_2$, $N = 9 \cdot 4\%$.

When a solution of the above ester (3 g.) and sodium methoxide (from sodium, $0 \cdot 8$ g.) in methyl alcohol (100 ml.) were heated in a sealed copper vessel at 100° for 80 minutes, rearrangement occurred in the expected manner, and the ethyl radical of the ester group was

replaced by a methyl group. After concentrating to a small bulk
the cooled brown solution was diluted with a little water, filtered,
acidified with acetic acid, and then vigorously scratched. The product
(2 g.) slowly crystallised. Recrystallised from alcohol, it formed
minute yellow prisms, which commenced to sinter and char about 235°,
but did not melt completely below 300°.

Found : C=63·1, H=4·3, N=9·7% ; calculated for $C_{15}H_{12}O_4N_2$,
C=63·4, H=4·2, N=9·9%.

The substance is most probably methyl 5-methyl-1 : 4-diketo-
7 : 8-benzo-1 : 2 : 3 : 4-tetrahydro-3 : 6-naphthyridine-2-carboxylate
(VIII).

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ISOLATION OF A TOXIC PRINCIPLE FROM THE SEEDS OF *MACROZAMIA SPIRALIS*.

By JOYCE M. COOPER, B.Sc.

Macrozamia spiralis (Cycadaceæ), commonly known as "Burrawang Palm", is one of some fifteen species of the genus *Macrozamia*, which is limited to Australia. It is widely distributed throughout the eastern areas from southern Queensland to the Victorian border of New South Wales. It is a small palm-like plant bearing red coloured cones, which when ripe split into a number of seeds or nuts. Both the leaves and seeds have frequently been reported as poisonous, producing two distinct types of poisoning. The seeds are known to be poisonous to man as well as to cattle, sheep, pigs, rabbits, and guinea-pigs. The aborigines used the seeds for food, but they appear to have appreciated the poisonous nature of the kernels, which were pounded, washed, and roasted before they were eaten.

Several workers have investigated the different parts of the plant, and have attempted to isolate and identify the toxic constituent or constituents. The seeds were investigated in 1876 by Norrie,[1] who separated potassium binoxalate and considered this to be the poisonous substance. Lauterer,[2] in 1895 and 1898, ascribed the toxic properties of the seeds and leaves to a resin. Guthrie,[3] in 1917, found no clearly defined toxic substance in the seeds, and concluded that the "toxin" was volatile. Dr. James Petrie[4] also investigated the various parts of the plant and in 1920 published his results and a summary of the work carried out by previous workers. Seddon, King, and Belschner in 1930[5] concluded from a series of experiments on the seeds that "the 'toxin' is a specific protoplasmic poison having a selective action on endothelial cells". Recently (1938) workers in the Department of Mines, Western Australia, investigated the species *M. Fraseri*,[6] but did not isolate an active constituent.

In the Coonabarabran district in 1929,[7] 2,200 out of 6,000 travelling sheep were lost as a result of their eating

the nuts of plants identified at that time as *Macrozamia spiralis.* (More recently it has been suggested that the species was probably *M. heteromera.*) Following this the Poison Plants Committee of the C.S.I.R., the University of Sydney and the N.S.W. Department of Agriculture began an investigation of the seeds, but, unfortunately, the work had to be discontinued through lack of funds before appreciable progress could be made. Investigations have been resumed recently. An aqueous extract was shown to be poisonous to sheep and guinea-pigs, and from such an extract a crystalline substance has now been isolated. The substance is found to be toxic to guinea-pigs when administered orally, but produces no ill effect when injected subcutaneously. This is of interest, as previous workers have reported that toxic symptoms could be produced only by oral administration of extracts of the seeds and not by hypodermic injection.

The material used for the isolation of the active crystalline substance was collected in the Moruya district by Mr. W. L. Hindmarsh, Director of Glenfield Veterinary Research Station, under whose care the feeding tests with sheep have been conducted for the Poison Plants Committee. Four ounces of the kernels (that is the kernels from about twenty seeds) was found to be a toxic dose for a sheep.

Isolation of the Toxic Substance.

The following is a typical example of the method which has been used in the isolation of the toxic substance.

6,320 grams of kernels (the only portion of the nuts which is known to be toxic), moisture content approximately 49%, were minced and macerated for two hours in six litres of water. The liquid, which contained starch in suspension, was separated by straining through muslin, the insoluble portion was washed three times with four litres of water and was then shown to be non-toxic. The washings were bulked with the first watery extract and allowed to stand overnight in a tall vessel ; the starch subsided as a compact mass, and the liquid was siphoned off. The starchy residue was washed with water and the washings were added to the siphoned liquid and the whole boiled. The protein present coagulated as a grey mass, which rose to the surface of the now clear yellowish solution, and was removed by straining through fine linen. Pressed free from extract and washed with water, the coagulated protein was found to be non-toxic. The clear solution

was then concentrated under reduced pressure at a temperature not exceeding 60° C. This method was chosen in preference to evaporation at ordinary pressure as certain constituents of the extract discoloured very readily. The concentrated solution (volume 1,400 mils) was light brown, opaque, and syrupy. To remove the last traces of protein it was treated with three volumes of 95% alcohol. A non-toxic amorphous precipitate was produced. The dilute alcohol solution was separated and concentrated under reduced pressure to a pale yellow syrup measuring 230 mils. Four volumes of 95% alcohol were added and a thick syrup (A) was precipitated. The clear liquid was decanted from this after two hours, and overnight 19 gm. of crystalline material separated. The mother liquor, concentrated under reduced pressure to 130 mils, and diluted with four volumes of absolute alcohol, gave a small amount of syrup and a further seven grams of crystals. The syrup (A) crystallised on standing, and by dissolving this in water and adding alcohol a further 19 gm. of crystals were obtained. The crude product (weight = 45 gm.) was washed well with absolute alcohol, and recrystallised by adding three volumes of absolute alcohol to its aqueous solution. The product was recrystallised four times by this method. It consisted of colourless triangular crystals, which did not melt sharply, but darkened at 196° C. and decomposed at 199° C. The following figures show the weights (calculated on materials dried at 100° C.) of starch, protein (heat coagulated), insoluble material, and dissolved substances in the above experiment.

Wt. of fresh kernels	..	..	6,320 gm.
Wt. of water (49%)	..	..	3,096 ,,
Wt. of starch	..	..	1,734 ,,
Wt. of coagulated protein	..	..	255 ,,
Wt. of insoluble material (other than starch)	..	..	800 ,,
Wt. of solids (including crystals, 45 gm.) in aqueous extract (by difference)	..	..	435 ,,

The same crystalline toxic substance was obtained by macerating 1 kg. of minced kernels (water content 49%) with 730 mils of 95% alcohol for a short period and then running off the aqueous-alcohol solution (about 60% alcohol). This solution on concentration and fractionation with alcohol gave a small yield of crystals.

The crystalline substance, for which the name Macrozamin is suggested, has the following properties. It is readily soluble in water, sparingly soluble in hot glacial acetic acid, and practically insoluble in absolute ethyl alcohol, methyl alcohol, ethyl acetate, acetone, ether petroleum ether, chloroform, and benzene. It shows no loss of weight when dried for three days over sulphuric acid or for $3 \cdot 5$ hours at $120° C$.

Found : $C = 40 \cdot 3\%$, $H = 6 \cdot 9\%$, $N = 7 \cdot 9\%$; $C_6H_{11}O_5N$ requires, $C = 40 \cdot 68\%$, $H = 6 \cdot 26\%$, $N = 7 \cdot 91\%$. $C_6H_{13}O_5N$, requires $C = 40 \cdot 21\%$, $H = 7 \cdot 31\%$, $N = 7 \cdot 82\%$.

Found : $\{\alpha\}_D^{21 \cdot 5° C.} = -74 \cdot 8°$.

Macrozamin can be acetylated and benzoylated, but these derivatives are difficult to purify and have not yet been obtained in a pure state. It gives Molisch's reaction for carbohydrates and after hydrolysis with 5% hydrochloric acid yields an osazone. Hydrolysis with dilute sodium hydroxide followed by acidification yields hydrocyanic acid, but no hydrocyanic acid is produced by hydrolysis with acids, almonds, or yeast. Work on its constitution is in progress, and it is hoped that a further paper will be ready at an early date.

TOXICITY OF MACROZAMIN.

The following tests were carried out by Professor Priestley, whose help is gratefully acknowledged.

When guinea-pigs were injected subcutaneously with an aqueous solution of the crystals equivalent to 1 gm./kilo body weight, no ill effect was produced. When a similar amount was given orally the animals died after 12-18 hours, and except for marked congestion of the lungs there were no post-mortem changes. One animal which was observed throughout the entire test (most animals died overnight) exhibited strychnine-like fits. In most cases the eyes of the test animals became swollen, watery and red.

SUMMARY.

The paper deals with the isolation of a crystalline substance from the kernels of the seeds of *Macrozamia spiralis*. It is toxic to guinea-pigs when administered orally, but not when injected subcutaneously.

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COORDINATION COMPOUNDS WITH FURFURALD-OXIME AS A CHELATE GROUP.

PART III. COMPLEX METALLIC DERIVATIVES OF β (ANTI) FURFURALDOXIME.

By A. BRYSON, M.Sc., B.App.Sc.,
and F. P. DWYER, M.Sc.

Since β furfuraldoxime has the anti structure (I) (Brady, *J. Chem. Soc.*, 1927, 1959), steric considerations preclude the formation of the usual monomeric chelated metallic derivatives in which the metal is always joined to the nitrogen of the oxime group, and the link must be metal to oxygen, (II).
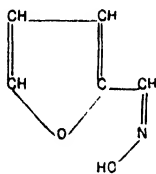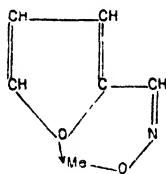
Whilst the oxime does form inner complex derivatives with many metals, there appears, however, to be some resistance to the formation of compounds of type II, and in many cases the orthodox N/metal link tends to be achieved by the formation of binuclear complexes, often containing three oxime groups, or of complexes with four oxime groups associated with the central bivalent metal. The complex acids formed in these cases often exhibit noteworthy stability, and yield water-soluble alkali metal salts. With Pt^{II}, Ni^{II} and Pd^{II} in the tris and tetrakis oxime derivatives, for reasons dealt with in the individual discussion on the metals, it appears that the metal is always four covalent, two or more of the possible links to the furane oxygen being inoperative. In the remarkably stable

cobaltic complex, however, this oxygen is indubitably linked, as also in the bridged binuclear complexes.

The complex acids with one hydrogen functioning as a univalent cation are remarkably analogous to the ferrous complexes with certain isonitrosoketones such as isonitroso-acetyl acetone (III) described by Kuster, Erfle, Roll and Schiller (*Z. physiol. Chem.*, 1926, 155, 157).

$$CH_3 \cdot \overset{\overset{\displaystyle \|}{\displaystyle O}}{C} \underset{}{\text{---}} \overset{\overset{\displaystyle \|}{\displaystyle N}}{C} \underset{}{\text{---}} \overset{\overset{\displaystyle \|}{\displaystyle O}}{C} \cdot CH_3$$

$$\overset{}{\underset{\displaystyle OH}{\diagdown}}$$
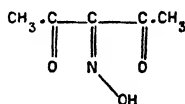
III

These complexes have the properties of weak or pseudo acids, have the general formula $H(Fe^{II}(R.CO.C{=}NO.CO.R')_3)$, and have been designated as six-covalent ferrous complexes. Magnetic measurements (Jacini, *Gazz. chim. ital.*, 1939, 69, 714) show them to be weakly paramagnetic ($\mu = 0 \cdot 59$ to $0 \cdot 75$) and it is concluded that they are of the $K_2Ba(Fe^{II}(NO_2)_6)$ type and hence have an octahedral structure. Although no ferrous furfuraldoxime complex could be prepared, it appears from the close analogy with the platinum, nickel and palladium compounds, that the ferrous isonitroso complexes should be formulated as four-covalent.

Palladium Compounds. Addition of the oxime to a hydrochloric acid solution of sodium chloropalladite gave immediately the pale yellow bisfurfuraldoxime palladous chloride. This substance, although initially easily soluble in acetone, became soluble in boiling acetone only after crystallisation. In boiling solution it was partly dissociated with darkening of the colour, and thus the molecular complexity could not be determined. The two forms were apparently the cis and trans isomers (IV), (V). The compound was soluble in aqueous alkali.
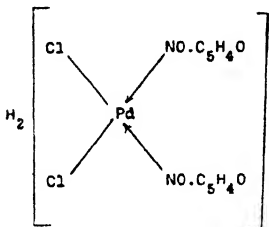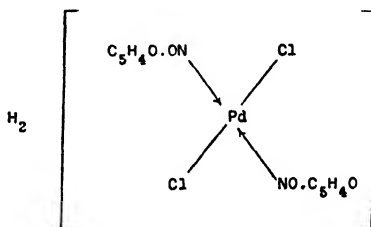
IV   V

With sodium acetate in boiling acetone/methanol solution the two chlorine atoms were eliminated with the formation of the darker yellow, highly insoluble bisfurfuraldoxime palladium (VI).
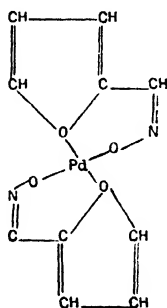
VI

With hot pyridine (VI) slowly dissolved, to give lemon yellow needles of bis pyridine bisfurfuraldoxime palladium, on cooling. This compound was freely soluble in organic media such as chloroform and also in water, and can presumably exist in the covalent form (VII) or in the oximate form (VIII) in aqueous solution. Proof of structure (VIII) is afforded by the transformation into bispyridine palladous chloride by treatment with cold dilute hydrochloric acid.

VII

$$(Pd(C_5H_5N)_2.(H_2O)_2)^{++}. (C_5H_4O.ON)_2$$
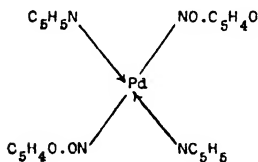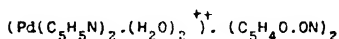
VIII

By boiling bispyridine bisfurfuraldoxime palladium (VII) with methyl alcohol or water, pyridine was eliminated and (VI) was regenerated. With one molecule of the oxime and refluxing in chloroform solution, bisfurfuraldoxime palladium dissolved, and gave on precipitation the bright yellow acidic tris furfuraldoxime palladium (IX), which was monomeric in boiling chloroform. This

compound is most probably 4-covalent. If 6-covalent, it should exist in two isomeric forms and by replacement of one oxime group with pyridine or ethylenediamine should yield a number of isomeric substitution products in each case. Although a second compound of the same empirical formula was isolated later, it proved to be dimeric. By treatment with pyridine (IX) gave only one bispyridine derivative identical with (VII) above ; and with ethylenediamine one monoethylenediamine bisfurfuraldoxime palladium complex—one molecule of the oxime being eliminated in each case.

The mechanism of formation of the tris compound from the bis compound is probably the opening of one of the chelate rings in (VI) with the addition of the new oxime group in the vacant coordination position. By its mode of formation from the coordinately saturated bis compound (VI), the tris compound must have one oxime group acting as a chelate group. The mode of attachment of the other two groups is uncertain, but from general principles it would appear that the link is through the nitrogen of the oxime group. This is supported by methylation experiments with methyl iodide and sodium methoxide, when (IX) gave the bis compound (VI) and O-methyl furfuraldoxime (X). No trace of the isomeric N-methyl furfuraldoxime (XI) could be detected.
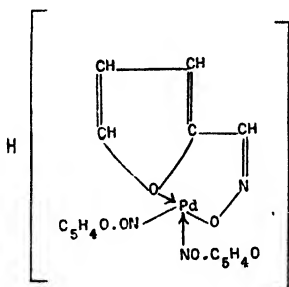
IX
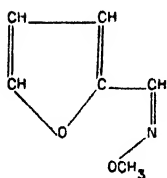
X
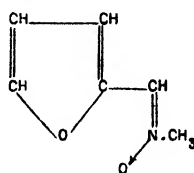
XI

Treated with excess of the oxime in chloroform solution the tris compound immediately gave an almost white precipitate of the acidic tetrakis compound (XII).

$$H_2 \left[\begin{array}{c} C_5H_4O.ON \qquad NO.C_5H_4O \\ Pd \\ C_5H_4O.ON \qquad NO.C_5H_4O \end{array} \right]$$
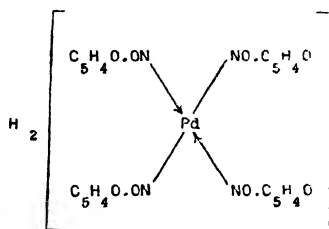
XII

In neutral solution in the presence of a very large excess of sodium acetate, the addition of the oxime (2 mols.) to a solution of sodium chloropalladite gave a precipitate of the same empirical formula as (IX), $Pd(C_5H_4O.ON)_2.C_5H_4O.NOH$; whilst approximately a third of the palladium remained in solution unchanged. Under no conditions could the bis compound (VI), $Pd(C_5H_4O.ON)_2$, be obtained directly. The precipitate obtained above was separated into two fractions—one very sparingly soluble in benzene and identical with (IX) above, and the other extremely soluble in benzene. The soluble form which was dimeric in freezing benzene, and changed rapidly in solution or in the solid state to (IX) was assigned the constitution (XIII).

$$H_2 \left[\begin{array}{c} C_5H_4O.ON \qquad OC_5H_4.ON \qquad NO.C_5H_4O \\ Pd \qquad\qquad Pd \\ C_5H_4O.ON \qquad NO.C_5H_4O \qquad NO.C_5H_4O \end{array} \right]$$
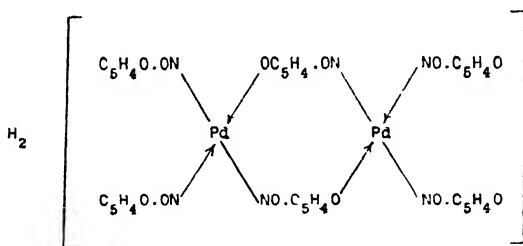
XIII

Compound (XIII) was soluble in dilute caustic soda, and regenerated a mixture of (IX) and (XIII) on acidification with acetic acid. It gave the same bispyridine and monoethylenediamine compound as (IX), and reacted, although more slowly, with one molecule of additional oxime to yield a tetrakis compound identical with (XII).

Platinum Compounds. The reaction between the oxime and solutions of platinous chloride was apparently peculiarly dependent on very precise conditions of acidity and concentration. Individual preparative procedures were difficult to repeat, and, in general, a mixture of a number of different compounds in varying proportions, resulted. By treating a solution of sodium chloroplatinite with the oxime (3 mols.) and keeping the mixture near the boiling point for some time a pale brown precipitate of indefinite composition was obtained. When dissolved in a mixture of acetone and concentrated hydrochloric acid a brown solution resulted, which on evaporation gave bis furfuraldoxime platinous chloride (XIV). This substance acted as a complex acid of considerable stability and was readily soluble in aqueous caustic soda, from which it was precipitated almost unchanged with acetic acid. The completely covalent nature of the substance was shown by the failure of zinc to precipitate any of the platinum by standing in contact with the aqueous acetone solution for several days. This compound probably has the same constitution as the palladous compound (V).

By refluxing with methyl alcoholic sodium acetate and acetone for several hours (XIV) was slowly decomposed and the bis compound $Pt(C_5H_4O.ON)_2$ (XV) was deposited in small amount. Like the palladous compound (VI) with which it is constitutionally similar, (XV) was very sparingly soluble in organic media, and could not be prepared directly by the addition of the oxime to platinous salt solutions. Attempts to prepare it in the absence of chloride, as from sodium platinonitrite, were also fruitless.

When bis furfuraldoxime platinous chloride was refluxed in alcoholic/acetone solution with excess of the oxime and sodium acetate, it gave the light buff, tetrakis furfuraldoxime platinum $H_2(Pt(C_5H_4O.NO)_4)$ (XVI), which was soluble in aqueous alkali and reprecipitated unchanged by acetic acid or ammonium chloride. The constitution of (XVI) is similar to the palladous compound (XII).

By solution of (XVI) in warm pyridine and cooling, bispyridine bisfurfuraldoxime platinum $(Pt(C_5H_5N)_2(C_5H_4O.ON)_2)$ (XVII) was obtained, two molecules of oxime being eliminated in the reaction.

Trisfurfuraldoxime platinum $Pt(C_5H_4O.ON)_2.C_5H_4O.NOH$ (XVIII) was obtained by dissolving the soluble portion of the reaction between sodium chlorplatinite and the oxime (3 mols.) in benzene, and fractionally precipitating with

petroleum ether. The most soluble portion was a pale yellow powder of the correct composition. Like the palladous compound (XIII) with which it is probably analogous by reason of its high solubility, tris furfuraldoxime platinum was soluble in caustic soda, and reacted with one mol. of oxime to yield a tetrakis compound identical with (XVI).

Owing to the difficulty of preparing pure compounds no isomeric forms were detected in the platinum series.

Nickel Compounds. As with palladium and platinum, the bis compound could not be isolated directly, but the greyish white tris furfuraldoxime nickel $Ni(C_5H_4O.ON)_2.C_5H_4O.NOH$ (XIX) was always obtained by the addition of the oxime to solutions of nickel acetate in the presence of sodium acetate or ammonium hydroxide. This substance was extremely soluble in organic media, and, since it was dimeric in benzene, is of the same type as the palladium compound (XIII). Unlike the corresponding platinum and palladium compounds (XIX), was somewhat unstable, being decomposed by acetic acid. No alkali metal salt was obtained, but the compound was degraded to the bis compound $Ni(C_5H_4O.ON)_2$ (XX). The yellowish brown bis compound also resulted by dissolving the tris compound (XIX) in cold pyridine and precipitating with water. One molecule of the oxime was eliminated partly as the oxime itself and partly as the isomeric furamide $C_4H_3O.CONH_2$. With large amounts of the tris compound the reaction with pyridine was more complex, and yielded, in addition to the bis compound, greenish-white basic salts.

In benzene, at the ordinary temperature, the tris compound (XIX) underwent slow decomposition with the separation of a highly insoluble substance (XXI) of the same empirical formula, as well as approximately an equal weight of the bis compound (XX). The eliminated oxime was partly transformed into furamide.

Addition of ethylenediamine in benzene to the tris compound (XIX) gave the monoethylenediamine derivative $Ni(C_5H_4O.ON)_2.C_2H_8N_2$ (XXII). The expelled oxime was recovered almost entirely as furamide.

With one molecule of oxime the tris compound (XIX) reacted to give the tetrakis compound $H_2.Ni(C_5H_4O.ON)_4$ (XXIII), which was decomposed by caustic soda, but was monomeric in benzene, and hence constituted like the palladium compound (XII).

Cobalt Compounds. Addition of the oxime to cobaltous acetate in the presence of sulphurous acid followed by the addition of ammonium hydroxide gave the unstable pink bis compound $Co(C_5H_4O.ON)_2$ (XXIV), which was oxidised rapidly in the air to the brown cobaltic compound $Co(C_5H_4O.ON)_3$ (XXV). This latter substance could be prepared by a variety of methods, and demonstrated quite strong coordination by the oxime group. Thus the oxime reacted rapidly with sodium cobalti-nitrite, as well as the following cobaltic ammines : carbonate tetrammine cobaltic sulphate, diaquotetrammine cobaltic chloride, and hexammine cobaltic chloride. The brown cobaltic compound was quite stable to cold concentrated hydrochloric acid and dissolved only slowly on heating, and was quite unaffected by concentrated ammonia solutions, pyridine or ethylenediamine. It is thus a 6-covalent complex with the three oxime groups acting as chelate groups. Like trisglycine cobalt, it should exist in two isomeric forms, and small amounts of a second isomer have been detected.

Copper Compounds. The only copper compound isolated was the green amorphous substance $Cu(OH).C_5H_4O.ON$ (XXVI), which was sparingly soluble in organic media, but dissolved easily in cold pyridine to a deep green solution, from which it was precipitated unchanged by water. The compound was quite unaffected by concentrated ammonia, or ethylenediamine, and hence must be considered as coordinately saturated. A diol bridge structure is proposed.
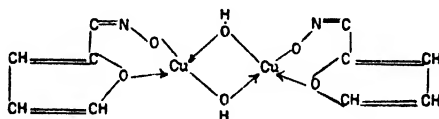
XXVI

Although the bis compound $Cu(C_5H_4O.ON)_2$ was not isolated, there is some evidence for its existence. Thus if bis furfuraldoxime cupric chloride (Bryson and Dwyer, THIS JOURNAL, 1940, *74*, 107) in acetone solution was treated with alcoholic sodium acetate, a greenish brown solution resulted. Evaporation of the solvent, or the addition of water or ether always gave the green hydroxy compound. The greenish brown solution probably contained the bis compound.

EXPERIMENTAL.

Bis Furfuraldoxime Palladous Chloride. IV, V. β furfuraldoxime was prepared by the method of Brady (*loc. cit.*) and freed from traces of the α isomer by solution in 5 N hydrochloric acid and then pouring into cold sodium carbonate to reprecipitate the oxime. After crystallisation from hot water, the pure oxime melted at 91-92°.

Sodium chloropalladite (0·5 gm.) in 30 mls. of water was treated with 10 mls. of 5 N hydrochloric acid, and the oxime (2 mols.) in alcohol was added. The yellow precipitate was easily soluble in acetone, but after crystallisation from warm aqueous acetone gave long yellow felted needles, which were then only sparingly soluble in acetone. The substance darkened in acetone solution on heating but became pale yellow on cooling. Owing to the dissociation, the molecular weight determinations were unsatisfactory.

Found : Pd = 26·58%, Cl = 17·7% ; calculated for $Pd(C_5H_4O.NOH)_2.Cl_2$, Pd = 26·68%, Cl = 17·76%.

Bis Furfuraldoxime Palladium. VI. The chloro compound above refluxed with sodium acetate in methyl alcohol-acetone solution for several hours gave a brownish yellow precipitate consisting of small rods and needles. The compound was only sparingly soluble in chloroform and quite insoluble in all other solvents. On heating it darkened, and decomposed with incandescence without melting. With alcoholic hydrochloric acid the original chloro compound was regenerated.

Found : Pd = 32·35% ; calculated for $Pd(C_5H_4O.ON)_2$, Pd = 32·45%.

Bis Pyridine Bisfurfuraldoxime Palladium. VII, VIII. Bis furfuraldoxime palladium was insoluble in cold pyridine but dissolved on boiling, and the yellow solution on cooling and the addition of petroleum ether gave bundles of lemon yellow needles of the bis pyridine derivative. This substance was soluble in most organic solvents and also in water. From the latter solution, by the addition of cold normal hydrochloric acid, a white precipitate of bis pyridine palladous chloride was obtained. When dissolved in water or alcohol and refluxed for some time pyridine was eliminated, and the original bis furfuraldoxime palladium was regenerated.

Found : Pd = 21·98%, C_5H_5N = 32·72% ; calculated for $Pd(C_5H_4O.ON)_2.2C_5H_5N$, Pd = 22·02%, C_5H_5N = 32·60%.

Tris Furfuraldoxime Palladium, Monomeric Form. IX. The bis compound (VI) was suspended in chloroform and refluxed with exactly one mol. of the oxime. After refluxing for some hours, when almost all of the bis compound had dissolved, the solution was cooled and filtered. Addition of petroleum ether then gave yellow monoclinic plates and rods of the tris compound, easily soluble in chloroform, and in boiling benzene. The substance dissolved in aqueous alcoholic alkali, but on acidification with acetic acid gave a mixture of the

monomeric and dimeric forms of the tris compound. The compound reacted immediately with warm pyridine to give the bis pyridine complex, one molecule of oxime being left in solution. With alcoholic hydrochloric acid the chloro compound (V) was formed.

Found: Pd$=24\cdot46\%$; mol. wt. in chloroform, ebullioscopic$=$ 438, 440; calculated for H.Pd($C_5H_4O.ON)_3$, Pd$=24\cdot55\%$; mol. wt.$=437\cdot7$.

Tris Furfuraldoxime Palladium, Dimeric Form. XIII. A cold aqueous solution of sodium chloro-palladite containing $0\cdot5$ gm. palladium and 20 gm. of crystalline sodium acetate, in 50 mls. of solution was cooled to 4°. An ice cold solution of the oxime ($1\cdot53$ gm.) in methyl alcohol was added rapidly with good stirring. The mixture was then poured into 200 mls. of ice water, and the pale yellow precipitate filtered and washed with ice water. Without drying, the precipitate was extracted with cold benzene. The insoluble residue consisted of the monomeric form of the tris compound with a little of the tetrakis compound. The orange benzene solution of the dimeric form was quickly dried with calcium chloride, and precipitated with petroleum ether, when it gave the required compound as a micro-crystalline yellow powder. The substance was extremely soluble in acetone and chloroform but changed rapidly in solution and in the solid state to the more insoluble monomeric form. It dissolved completely in cold pyridine, but almost instantly gave a precipitate of the bis pyridine compound identical with (VII). One molecule of oxime eliminated in this reaction was recoverable from the pyridine. The molecular weight was determined cryoscopically in benzene on a freshly prepared sample, and a correction was applied for the insoluble monomeric form.

Found: Pd$=24\cdot55\%$; mol. wt.$=918$, 902; calculated for (H.Pd($C_5H_4O.ON)_3)_2$, Pd$=24\cdot55\%$, mol. wt.$=875$.

Tetrakis Furfuraldoxime Palladium. XII. A solution of tris furfuraldoxime palladium, either form, in chloroform treated with excess of the oxime gave an almost immediate, very pale yellow precipitate of the tetrakis compound. The substance was insoluble in benzene and acetone, but dissolved slowly in boiling chloroform to a yellow solution. During the process of solution the compound was partly dissociated, since on cooling only a small amount was re-deposited, whilst addition of petroleum ether gave a mixture of the tris and tetrakis compounds. It was soluble in alcoholic alkali, but acidification with acetic acid gave a mixture of the tris and tetrakis compounds. This was confirmed by microscopic tests and by analysis. The compound dissolved in hot pyridine, and gave the usual bis pyridine derivative (VII) on cooling.

Found: Pd$=19\cdot28\%$; calculated for H_2Pd($C_5H_4O.ON)_2$, Pd$=19\cdot31$.

(Pd, found after solution in NaOH) and reprecipitation with acetic acid $= 22 \cdot 45\%$.)

Ethylenediamine Bis Furfuraldoxime Palladium. Either form of the tris compound or the bis pyridine compound in chloroform solution was treated with anhydrous ethylenediamine in benzene. The resulting pale yellow precipitate of rosettes of needles was insoluble in organic solvents, but easily soluble in alcohol or water.

Found : Pd $= 27 \cdot 43\%$; calculated for $Pd(C_5H_4O.ON)_2.C_2H_8N_2$, Pd $= 27 \cdot 58\%$.

Methylation Experiments. The tris compound (IX) ($1 \cdot 0$ gm.) was added to 50 mls. of anhydrous methanol containing 1 mol. of sodium methoxide. Methyl iodide in slight excess was added to the resulting pale yellow solution of the sodium salt so obtained, and the mixture allowed to stand in the dark at room temperature for two days. At the end of this time a brownish yellow precipitate identified as the bis compound (VI) had separated. The solution had darkened considerably—due to the formation of palladous iodide—and had the powerful characteristic odour of O-methyl furfuraldoxime. Attempts to isolate this compound for positive identification were unsuccessful, but it was confirmed by comparison with the odour of an authentic sample of O-methyl furfuraldoxime prepared from the oxime itself, and methyl iodide in the presence of silver oxide (Brady, *J. Chem. Soc.*, 1926, 2386).

When the solution was boiled with aqueous caustic soda, no trace of methylamine could be detected—hence it was concluded that the N-methyl isomer was not formed during the reaction. The transformation of N-methyl aldoximes into methylamine by treatment with caustic soda is a general reaction, and was confirmed in this instance on a sample of N-methyl furfuraldoxime hydroidide prepared by allowing the oxime to stand with methyl iodide in the dark for a week (Brady, *loc. cit.*). Attempts to prepare a compound $Pd(C_5H_4O.ON)_2.C_5H_4O.NO.CH_3$ by reaction between the bis compound (VI) and either of the methyl derivatives of furfuraldoxime were fruitless. Apparently the stability of the tris compound is dependent upon the metal being in an anion, and is incapable of existence as a neutral complex in which the hydrogen is replaced by the methyl group.

Platinum Compounds.

Bis Furfuraldoxime Platinous Chloride. XIV. Potassium chloroplatinite ($1 \cdot 85$ gms.) was dissolved in water (50 mls.) and the oxime ($1 \cdot 5$ g.) added. The mixture became cloudy and sodium acetate was added and the solution warmed. The buff amorphous precipitate, which formed slowly, was filtered, and after washing was dissolved in a mixture of concentrated hydrochloric acid and acetone. The clear brown solution on slow evaporation gave light brown rods of the

required compound. The compound was soluble in aqueous caustic soda, and reprecipitated with acetic acid. Very little change occurred by this solution and reprecipitation, a trace only of chloride being found in the solution, whilst a little of the bis compound $Pt(C_5H_4O.ON)_2$ was formed.

Found :   Pt = 40·1%,   Cl = 14·23% ;   calculated   for $PtCl_2.2C_5H_4O.NOH$, Pt = 39·99%, Cl = 14·52%.

Bis Furfuraldoxime Platinum. XV. Bis furfuraldoxime platinous chloride was dissolved in acetone and refluxed with methyl alcoholic sodium acetate for ten hours. The small amount of light brown precipitate formed was well washed with acetone, and then with methyl alcohol and dried at 100°. The substance was also prepared by treating a solution of sodium platinonitrite with the oxime and sodium acetate, removing the buff precipitate of uncertain composition, dissolving in hot pyridine and allowing to cool. The resulting brown crystalline precipitate was heated for some hours at 120° to remove pyridine.

The compound was highly insoluble in all organic media except pyridine, and decomposed with incandescence on heating, without melting.

Found :   Pt = 47·4%,   47·05% ;   calculated   for $Pt(C_5H_4O.ON)_2$, Pt = 46·78%.

Tetrakis Furfuraldoxime Platinum. XVI. This substance was prepared in several ways : by the addition of a large excess of oxime to an acid solution of potassium chloroplatinite ; by the addition of an excess of oxime to the tris compound (XVIII, see later) ; or by refluxing bis furfuraldoxime platinous chloride (XIV) with methyl alcoholic sodium acetate and an excess of oxime. Prepared by any of these methods the compound is obtained as a light buff crystalline powder, insoluble in all organic solvents. It was easily soluble in aqueous alkali, and reprecipitated unchanged by the addition of acetic acid or ammonium chloride.

Found :   Pt = 30·92% ;   calculated   for $H_2Pt(C_5H_4O.ON)_4$, Pt = 30·63%.

Bis Pyridine Bis Furfuraldoxime Palladium. XVII. The tetrakis compound (XVI) was dissolved in hot pyridine and cooled. The brownish crystalline bis pyridine compound so obtained lost pyridine on heating and was transformed to the bis furfuraldoxime compound (XV), above.

Found : Pt = 34·01, 34·5% ; calculated for $Pt(C_5H_4O.ON)_2.2C_5H_5N$, Pt = 34·05%.

Tris Furfuraldoxime Platinum. XVIII. Potassium chloroplatinite (1·85 gms.) was dissolved in 50 mls. of water, and 1·5 gms. of the oxime added. Sodium acetate (30 gms.) in water 50 mls. was then added and the mixture heated at 90° for an hour. The resulting light

buff precipitate was removed, dried, and dissolved in hot benzene. After filtering an equal volume of petroleum ether was added to the light brown solution and the resulting brown precipitate of indefinite composition filtered off. The filtrate was then treated with an excess of petroleum ether, when it gave the required compound as a pale yellow precipitate. The tris compound was easily soluble in all organic solvents, and decomposed violently on heating, without melting. It was soluble in caustic soda, and reprecipitated by acid. Owing to the small amounts of material available, molecular weight determinations could not be undertaken. In analogy with the palladium compound (XIII), which showed a similar high solubility in benzene, it is probably dimeric.

Found : Pt=37·13% ; calculated for $(H.Pt(C_5H_4O.ON)_3)_2$, Pt= 37·09%.

Nickel Compounds.

Tris Furfuraldoxime Nickel-Soluble Form. XIX. The oxime (3·3 gms.) was dissolved in alcohol, and added to nickel acetate (2·1 gms.) in water 100 mls. The mixture was then heated to 80-90° and dilute ammonium hydroxide added carefully. The greyish white precipitate was washed several times with dilute alcohol, then with water, and dried at room temperature. The compound was extremely soluble in all organic solvents to dark brown solutions. It melted somewhat indefinitely 138-140° to a black gum. It was somewhat soluble in aqueous alcoholic alkali but soon deposited a precipitate, later identified as the bis compound.

Found : Ni=14·72%, 14·88% ; mol. wt. in benzene cryoscopic= 861, 845 ; calculated for $(H.Ni(C_5H_4O.ON)_3)_2$, Ni=15·07% ; mol. wt.=779.

Bis Furfuraldoxime Nickel. XX. (1) The tris compound was dissolved in cold pyridine, filtered, and cold water added. The semi colloidal yellowish precipitate which came down was coagulated by the addition of sodium acetate, and after filtration, washed well with water and dried at 100°. The yellowish brown bis compound was insoluble in benzene, and chloroform, but soluble in acetone.

Found : Ni=21·22% ; calculated for $Ni(C_5H_4O.ON)_2$, Ni=21·06%.

When the above reaction is performed with large amounts of material (10 gms.) and the reaction mixture is heated, greenish basic (?) compounds of indefinite composition are formed. These substances apparently contain pyridine as an essential part of the molecule, and temperatures of the order of 130-140° are required to remove it. In one experiment, an acetone-soluble compound was isolated which gave analyses very close to the compound $NiOH.C_5H_4O.ON.C_5H_5N$.

Found : Ni=22·24% ; calculated; Ni=22·18%.

Unlike the bis compound, this substance was green and soluble in chloroform. Subsequent attempts to repeat the preparation were unsuccessful.

(2) The tris compound (XIX) was dissolved in cold benzene so as to form an almost saturated solution, which was allowed to stand for several days. The greyish yellow precipitate which came down, after washing with benzene, was extracted with acetone, and the filtrate evaporated to dryness. The dry residue was washed with hot aqueous alcohol to remove oxime and furamide, and dried at 100°. It was identical with the bis compound as obtained above.

Found : Ni $= 20 \cdot 96 \%$.

Tris Furfuraldoxime Nickel—Insoluble Form. XXI. The precipitate formed by allowing the soluble form of the tris compound (XIX) to stand in benzene solution, as shown above, was extracted with acetone. The acetone-insoluble portion was washed with hot aqueous alcohol and dried. The pale greyish green compound was almost completely insoluble in all organic solvents. It melted somewhat indefinitely at 141° to a black gum. Owing to its insolubility, the molecular complexity could not be determined—but the compound is probably the analogue of the palladium compound (IX).

Found : Ni $= 15 \cdot 28 \%$; calculated for $H.Ni(C_5H_4O.ON)_3$, Ni $= 15 \cdot 07 \%$.

Tetrakis Furfuraldoxime Nickel. XXIII. The soluble form of the tris compound (XIX) was dissolved in benzene and treated with exactly one mol. of oxime. The solution after evaporation at room temperature gave a dark brown gum, which crystallised on scratching to brownish needles. The substance was ground up finely in a mortar with aqueous alcohol, and dried at room temperature. The substance was easily soluble in organic solvents, and was decomposed to the tris compound and oxime by boiling with aqueous alcohol.

Found : Ni $= 11 \cdot 90 \%$; mol. wt. in benzene cryoscopic $= 486$; calculated for $H_2Ni(C_5H_4O.ON)_4$, Ni $= 11 \cdot 76 \%$; mol. wt. $= 500 \cdot 7$.

Ethylenediamine Bis Furfuraldoxime Nickel. XXII. The soluble form of the tris compound (XIX) was dissolved in benzene, and exactly one mol. of ethylenediamine in benzene solution was added with constant shaking. The solution became lighter in colour, and after filtering off a small amount of precipitate was allowed to stand overnight, when a mixture of amber and white crystals was deposited. These were washed with hot aqueous alcohol, leaving well defined amber cubes of the required compound.

Found : Ni $= 17 \cdot 26 \%$; calculated for $Ni(C_5H_4O.ON)_2.C_2H_8N_2$, Ni $= 17 \cdot 33 \%$.

The aqueous alcoholic washings from above, on evaporation gave crystals of a white substance, m.p. 141°. On boiling with alkali,

ammonia was evolved, whilst the addition of bromine water and caustic soda gave a blue colour. These tests are characteristic of furamide $C_4H_4O.CONH_2$, and the identity was confirmed by a mixed melting point with an authentic sample of this substance.

An attempt to prepare the ethylenediamine derivative from the insoluble form of the tris compound (XXI) gave a similar product to that above, but it could not be obtained pure.

Found : $Ni = 16·6\%$.

Cobalt Compounds.

Bis Furfuraldoxime Cobalt. XXIV. To an aqueous solution of cobalt chloride hexahydrate (3·3 gms.) was added 15 mls. of 10% sulphurous acid, and the oxime (4·4 gms.) dissolved in alcohol, followed by dilute ammonium hydroxide until the solution was slightly alkaline. The resulting pink precipitate was filtered very rapidly, washed with ammonium sulphite and alcohol, and dried in an atmosphere of carbon dioxide. It was insoluble in water, and organic solvents, but dissolved easily in ammonium hydroxide solution yielding probably the diamine. It was particularly sensitive to oxidation, passing to the brown cobaltic compound.

Found : $Co = 21·22\%$; calculated for $Co(C_5H_4O.ON)_2$, $Co = 21·10\%$.

Tris Furfuraldoxime Cobalt. XXV. To a solution of cobaltous chloride hexahydrate (4 gms.) in water was added 20 mls. of 3% hydrogen peroxide, and the oxime (excess) in alcohol. Addition of sodium acetate then gave a chocolate brown precipitate, which was crystallised from benzene and petroleum ether to give a brown amorphous powder. The substance was also formed by warming a solution of the oxime with sodium cobaltinitrite, or with a large variety of cobalt amines. It was extremely soluble in chloroform, and acetone, but sparingly soluble in alcohol. A benzene solution on standing for some weeks deposited slowly an amorphous brown powder of a similar colour, which was soluble in chloroform. This substance was not formed in an amount sufficient for analysis, but was probably an isomeric form. The cobaltic compound (XXV) was quite unaffected by concentrated ammonia, in which it was quite insoluble, or ethylenediamine. It was recovered unchanged from its solution in pyridine by the addition of water. It was not attacked by concentrated hydrochloric acid except on prolonged boiling.

Found : $Co = 15·0\%$; calculated for $Co(C_5H_4O.ON)_3$, $Co = 15·14\%$.

Copper Compounds.

Diol Bisfurfuraldoxime Copper. Cupric chloride dihydrate (3·4 gms.) was dissolved in methyl alcohol, and the oxime (3·0 gms.) added, followed by methyl alcoholic sodium acetate. A dark brown solution resulted, which on the addition of water or ether gave a dark green

precipitate. This was washed with alcohol and water, and dried at 100°. The same substance was obtained by the addition of the oxime to aqueous copper salt solutions, followed by ammonium hydroxide or sodium acetate, but the preparations were always contaminated by traces of other basic salts. The compound was slightly soluble in acetone, alcohol, and benzene, but easily soluble in pyridine, from which it was reprecipitated by water. The reprecipitated material contained no coordinated pyridine. Similarly it failed to react with concentrated ammonia, or with a benzene solution of ethylenediamine. The molecular weight was determined in pyridine solution by Rast's method (*Ber.*, 1921, *54*, 1979), using azobenzene as a comparison standard, and showed the compound to be probably dimeric.

Found : $Cu = 33 \cdot 2\%$; calculated for $(Cu.OH.(C_5H_4O.ON))_2$, $Cu = 33 \cdot 30\%$.

Bis Furfuraldoxime Copper. Attempts to prepare this compound were fruitless, the green compound always being isolated. When the green compound was heated for some time with an acetone solution of the oxime in very large excess, it dissolved partly to a brownish green solution, which, however, deposited the original green compound on standing for a short time. The deposited material was not soluble in oxime-free acetone, hence it seems feasible that the required bis compound was formed momentarily and then decomposed.

In another attempt the green compound was dissolved in pyridine, oxime added, and the mixture warmed for a short time. On standing until the pyridine evaporated, the original green hydroxy compound was left mixed with a very large amount of furamide. It appears that the bis compound is formed under these conditions but decomposes, the oxime being eliminated in the process as furamide.

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A NOTE ON THE TRANSFORMATION OF β FURFURALDOXIME TO FURAMIDE.

By A. BRYSON, M.Sc., B.App.Sc.,
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In the previous paper (THIS JOURNAL, 1940, *74*, 455), a number of references were made to the transformation of β furfuraldoxime to the isomeric furamide (pyromucamide) by reactions which lead to the elimination of one molecule of oxime from tris furfuraldoxime nickel $(H.Ni(C_5H_4O.ON)_3)_2$. This transformation is particularly interesting in view of the similar reaction carried out with Raney nickel, and it seems valuable to give a few more explicit details of the reactions in which the transformation was found to occur.

Large amounts of the amide were obtained in the following cases by suitable treatment of the nickel compound :

   (1) By allowing an acetone solution to stand at room temperature for several weeks, whereby the tris compound was degraded to the bis compound $Ni(C_5H_4O.ON)_2$.

   (2) By the action of anhydrous ethylenediamine in benzene solution, whereby the monoethylenediamine derivative of the bis compound was precipitated.

Smaller amounts of amide contaminated with much oxime were obtained by :

   (1) Solution of the tris nickel compound in hot pyridine, followed by precipitation of the bis compound formed with water.

   (2) Allowing a benzene solution of the tris compound to stand at room temperature for a week.

   (3) By dissolving the tris compound in alcoholic ammonia, and allowing the mixture to stand exposed to the air for three days.

During attempts to isolate the copper compound $Cu(C_5H_4O.ON)_2$ by treatment of the hydroxy compound $Cu.OH.(C_5H_4O.ON)$ with excess of oxime, large amounts of amide were obtained by each of the following two procedures :

(1) The hydroxy compound was dissolved in pyridine containing a large excess of oxime, the mixture boiled for an hour and then allowed to stand in the air until all the pyridine evaporated.

(2) The hydroxy compound was refluxed in acetone with excess of the oxime, and methyl alcoholic sodium acetate for some hours.

The method of isolation of the amide in all cases was similar, and consisted in evaporation of the products of reaction to dryness followed by extraction with warm 20% alcohol. The resulting solution of oxime and amide was treated with excess of copper sulphate solution, followed by dilute ammonium hydroxide. The precipitated green copper hydroxy compound of the oxime was filtered off, and the filtrate evaporated to dryness. Extraction with hot acetone then removed the soluble amide. After identification by a mixed melting point on the first sample, all subsequent tests were carried out by the addition of bromine water and caustic soda, which gives a deep blue colour, changing in a few minutes to a reddish violet.

The analogous platinum and palladium tris compounds, however, gave no evidence of the oxime/amide transformation when tested by any of the procedures above. The failure of the reaction with these metals is apparently due to the high stability of the complexes—the loose coordination of oxime to metal which is characteristic of the tris and tetrakis nickel compounds and the bis copper compound being essential to the transformation.

The Catalytic Transformation of β Furfuraldoxime to Furamide.

Bis furfuraldoxime nickel (10 mg.), $Ni(C_5H_4O.ON)_2$ was suspended in benzene, and the oxime (0·2 gm.) added. On warming the bis compound dissolved to a brown solution of the tetrakis compound, and the mixture was allowed to stand for a week in a stoppered test-tube. At the end of this time, approximately 0·1 gm. of white micaceous crystals of the amide had deposited. The reaction is apparently the successive formation and

decomposition of the tetrakis compound with the elimination of amide :

$$Ni(C_5H_4O.ON)_2 + 2C_5H_4O.NOH \rightarrow H_2Ni(C_5H_4O.ON)_4$$
$$H_2Ni(C_5H_4O.ON)_4 \rightarrow 2C_4H_3O.CONH_2 + Ni(C_5H_4O.ON)_2.$$

The Action of Raney Nickel on Aldoximes.

The transformation of aldoximes to the corresponding amides was first recorded by Paul (*Compt. rend.*, 1937, *204*, 363 ; *Bull. Soc. chim.*, 1937, (5), *4*, 1115 ; *Chem. Abs.*, 1937, *31*, 3003, 8506), using Raney nickel at 100° in various solvents. With β furfuraldoxime the reaction was slow at room temperature, but in alcoholic solution at 100° and 80% yield of furamide was obtained, whilst with the oxime alone, an exothermal reaction occurred which was complete in a few minutes.

The suggestion was made that the nickel formed an oxime complex in which the O.N link in the oxime was weakened, facilitating rearrangement, which was catalysed by traces of iron and aluminium in the Raney nickel. This was supported by the observation that some of the nickel appeared to dissolve to a red solution.

The transformation of oximes to the corresponding acids and ammonia by boiling with aqueous caustic soda has been recorded by Jordon and Hauser (*J. Am. Chem. Soc.*, 1936, 1304). In particular, with β furfuraldoxime at 97-100° for 10 minutes a 49% yield of furoic (pyromucic) acid was obtained. The suggested mechanism was the dehydration of the oxime to nitrile, followed by hydration of the nitrile to the acid.

The experiments carried out by the authors support the mechanism proposed by Paul in so far as the formation of a nickel complex is concerned, but suggest that further catalytic intervention by iron or aluminium is unnecessary. The reaction with Raney nickel appears to be the formation of a complex acid, probably $H_2Ni(R.ON)_4$, which is successively decomposed to the bis compound and amide, and reformed.

Since only β aldoximes can generally form coordination compounds with metallic salts (Hieber and Leutert, *Ber.*, 1929, *62B*, 1839), the reaction is obviously a trans Beckmann transformation, and in those cases where α aldoximes were used, an α→β change probably preceded the formation of the intermediate nickel complex.

In no case during these experiments was any trace of furfuronitrile detected, and there appear to be no grounds

for assuming that the transformation proceeds in any case via the nitrile. Indeed, in the experiments of Jordon and Hauser, it appears that aldoximes are transformed to amides under the influence of hot alkali, which then hydrolyses the amide to the acid and ammonia.

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MAGNETIC STUDIES OF COORDINATION COMPOUNDS.

PART III. FACTORS AFFECTING THE NATURE OF BONDS BETWEEN NICKEL AND CERTAIN NON-METALLIC ATOMS.

By D. P. MELLOR, M.Sc. and D. P. CRAIG.

It is now well known from different lines of investigation that diamagnetic quadricovalent nickel complexes are square coordinated. All nickel complexes in which the metal has a coordination number of four do not, however, fall into the diamagnetic, square class. Nickel bis-acetylacetone (Fig. 1) for example, is paramagnetic, with a
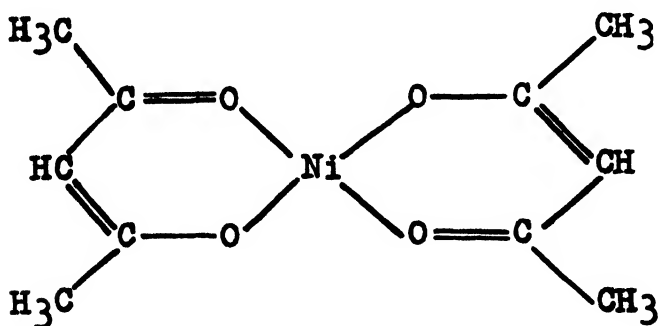
Fig. 1.

moment of $3 \cdot 2$ Bohr magnetons which,[1] after allowing for a small orbital contribution, corresponds to the existence of two unpaired electron spins in the nickel atom. This, as indicated in Fig. 2A, is the number of unpaired electrons in the nickel ion itself.

The observation that the nickel atom in bis-acetyl-acetone nickel possesses two unpaired electrons has been interpreted by Pauling[2] to mean that the four bonds linking nickel to oxygen are tetrahedral ionic or sp^3 bonds.* When, however, a nickel atom is linked to other atoms by four electron pair bonds, an electronic rearrangement occurs which results in the disappearance of the unpaired electron spins and at the same time the disappearance of paramagnetism. The outer electronic structure of square coordinated nickel is represented diagrammatically in 2B.
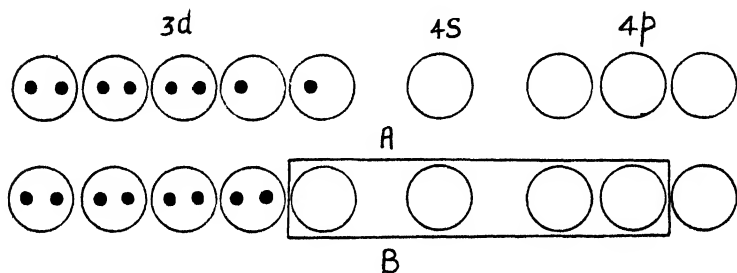
Fig. 2

It is a matter of some interest to investigate the factors that determine which of these modes of bonding (ionic, sp^3 or dsp^2) shall occur. Pauling and his collaborators have studied the occurrence of ionic and covalent bonding in octahedral complexes of Fe^{II} and Fe^{III}, especially those of biochemical importance,[3] but so far, little has been attempted in the way of a systematic study of the factors which affect bond type among the quadricoordinated complexes of Fe^{II}, Co^{II}, Mn^{II} and Ni^{II}. Cambi and his school have already accumulated magnetic data relating to complexes of these metals, including nickel[3] and where necessary this has been drawn upon to provide additional examples of some of the six types shortly to be described. Nickel has been chosen for the first portion of the survey, partly because it offers a case where a clear cut distinction can readily be drawn between square and tetrahedral

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* Magnetically, no distinction can be drawn between ionic and sp^3 bonds. Throughout this paper paramagnetic nickel complexes will, for the sake of brevity, be referred to as ionic or tetrahedral complexes.

bonding, and partly because, with the exception of copper, which does not lend itself to magnetic investigation of this kind,* nickel, of all the metals of the first transition series, most readily forms square complexes. This latter conclusion emerges from data already reported in the literature and from an, as yet, uncompleted survey of the other members of the first transition series (Co^{II}, Fe^{II} and Mn^{II}).

Following up clues already provided by the magnetic observations made on the octahedral complexes of Fe^{II}, Fe^{III} and Co^{III}, the present investigation has been directed mainly to the study of the influence of electro-negativity of linked atoms on bond character. Tables for the electro-negativity of most of the common elements have been drawn up by Pauling who has also deduced a relation showing the amount of ionic character to be expected for given differences in the electro-negativity of bonded atoms[2]; in general, it may be stated the greater the difference in electro-negativity the greater the amount of ionic character of a bond. With the atoms chosen in the present investigation, namely sulphur, nitrogen and oxygen, for which the electro-negativities are $2 \cdot 5$, $3 \cdot 0$ and $3 \cdot 5$ respectively, the tendency to form covalent complexes with nickel should be greatest with sulphur and least with oxygen. Electro-negativity considerations alone are insufficient to account for the magnetic properties of some nickel complexes. For example, it has been shown in a previous paper[4] that the marked deformation of Ni-N bond angles which occur in the nickel derivative of a suitably substituted pyrromethene, profoundly alters the magnetic character of the nickel atom. Hence it is necessary to consider the part played by this factor whenever there is reason for suspecting that large bond angle distortions occur.

In order to facilitate the discussion which follows and to indicate as clearly as possible the factors involved in determining bond type, the compounds studied have been classified in regard to the four atoms linked to nickel without any reference to the organic groups in which

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* Ionic and square complexes of Cu^{II} cannot readily be distinguished by magnetic measurements.

these atoms happen to occur.　Classes I-VI are as follows :
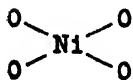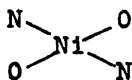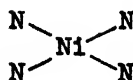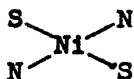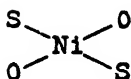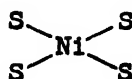
In tabulating the results, each class has been further subdivided according as the nickel forms part of a cation (or anion) or part of a neutral complex, usually referred to as an internal complex.　In the last subdivision, which comprises the majority of the compounds studied, two of the bonds to nickel are formed as a result of replacement of hydrogen atoms attached to the nitrogen, oxygen or sulphur atoms of the coordinating groups.　It is customary to represent these bonds by lines and the so-called coordination bonds by arrows.　Insofar as it permits one to keep track of the valencies this convention is helpful but it is misleading if it indicates any difference in the nature of the bonds.　There is no difference.

While in many cases there is no direct proof of the correctness of the structures attributed to the listed compounds (direct in the sense that the structures are based on complete X-ray or electron diffraction analyses or the synthesis of isomers, etc.) there is now such an extensive body of evidence relating to the structure of coordination compounds, especially those containing chelate rings,[5] that, in all but a few instances, reasonable structures can be formulated with some confidence in their correctness. These instances, which have been indicated in the discussion, arise where it is not possible to distinguish between two feasible modes of chelation.

The experimental results are set out in Tables I-VI, where each table deals with the class of the corresponding number.　For convenience in making references, the compounds themselves have been numbered.　The second

TABLE I. General Type:
$$O \diagdown \diagup O \atop O \diagup Ni \diagdown O$$

No.	Compound.	$\chi_M \times 10^{-6}$	μ
1	Bis acetylacetone nickel* $(CH_3.CO.CH.CO.CH_3)_2Ni$	4242	3·2
2	Bis nicotinylacetone nickel $(C_9H_6O_2N)_2Ni$..	3150	2·8
3	Bis salicylaldehyde nickel** $(O.C_6H_4.CHO)_2Ni$	4230	3·2
4	Potassium nickel oxalate $K_2[Ni(C_2O_4)_2]$	4410	3·2
5	Ammonium nickel malonate $(NH_4)_2[Ni(C_2H_2O_4)]$	4895	3·4

TABLE II. General Type:
$$N \diagdown \diagup O \atop O \diagup Ni \diagdown N$$

No.	Compound.	$\chi_M \times 10^{-6}$	μ
6	Bis α benzoin monoxime nickel $(C_6H_5C.N : O.CH.OH.C_6H_5)_2Ni.$	Dia- magnetic	0
7	Bis o-amino phenol nickel $(O.C_6H_4.NH_2)_2Ni.$	Dia- magnetic	0
8	Nicotinylacetone ethylenediamine nickel mono- hydrate, $(C_{20}H_{20}O_2N_4)NiH_2O$	Dia- magnetic	0
9	Bis salicylaldehyde ethylenediamine nickel $(O-C_6H_4.CH : en : CH.C_6H_4O)Ni$	Dia- magnetic	0
10	Bis salicyladoxime nickel** $(-O-C_6H_4.CH : NO)_2Ni$	Dia- magnetic	0
11	Bis salicylaldimine nickel** $(O-C_6H_4.CH : NH)_2Ni$	Dia- magnetic	0
12	Bis imino paonol nickel $(-O-C_6H_4.CH_2O.CH : NH)_2Ni$	Dia- magnetic	0
13	Bis benzene azo naphthol nickel $(-O-C_{10}H_4.N : N.C_6H_4)_2Ni$	Dia- magnetic	0
14	Bis 8 hydroxy quinoline nickel $(O-C_9H_7N)_2Ni$	4560	3 4
15	Bis α benzil monoxime nickel $(C_6H_5C : O.CN : O.C_6H_5)_2Ni$ ..	5590	3·6
16	Bis glycine nickel $(NH_2CH_2COO)_2Ni$	4330	3 2
17	Bis picolinic acid nickel $(N.C_5H_4COO)_2Ni$	4260	3·2
18	Bis semicarbazide nickel sulphate $[(O.NH_2.C : N.NH_2)_2Ni]SO_4$..	3660	3·0

TABLE III. General Type : $\begin{array}{c} N \diagdown \ N \\ Ni \\ N \diagup \ N \end{array}$

No.	Substance.	$\chi_M \times 10^{-6}$	μ
19	Bis naphthoquinone dioxime nickel ($C_{10}H_5NO.NOH)_2Ni$ ..	Dia-magnetic	0
20	Bis 4 : 4¹ dimethyl diazoaminobenzene nickel‡ ($CH_3.C_6H_4.NH.N : N.C_6H_4.CH_3)_2Ni$ ..	Dia-magnetic	0
21	Bis diazoaminobenzene nickel‡ ($C_6H_5.NH.N : N.C_6H_5)_2Ni$ ..	Dia-magnetic	0
22	Bis 1 : 2 naphthalene diamine nickel acetate $[Ni(C_{10}H_6.NH_2.NH_2)_2](CH_3COO)_2$ ..	3550	3·0
23	Bis o-phenylene diamine nickel sulphate $[Ni(NH_2.C_6H_4.NH_2)_2]SO_4$ ..	3680	3·1
24	Bis 8-aminoquinoline nickel nitrate tetra-hydrate $[Ni(C_9H_6.N.NH_2)_2](NO_3)4H_2O$ ..	4442	3·2
25	Triethylene tetramine nickel sulphate $[Ni(NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2)]SO_4$	3443	2·9
26	Bis pyridylbenziminazole nickel chloride $[Ni(N_3C_{12}H_9)_2]Cl_2$ ..	4031	3·1
27	Bis 1 : 8 naphthalene diamine nickel sulphate $[Ni(C_{10}H_6.NH_2.NH_2)_2]SO_4$ ..	Dia-magnetic	0
28	Bis aminoguanidine nickel sulphate $[Ni(NH_2.NH : C.NH.NH_2)_2]SO_4$ ..	Dia-magnetic	0
29	Bis phenylethylenediamine nickel nitrate†* $Ni(C_6H_5.CH.NH_2.CH_2.NH_2)(NO_3)_2$..	Dia-magnetic	0
30	Potassium nickel succinimide* $K_2Ni(C_4H_4O_2NH)_4$ ..	Dia-magnetic	0

* Additional members of this class measured by other investigators include the nickel compounds formed with phthalocyanine, protoporphyrin, benzyl methyl and other glyoximes, etc. All are diamagnetic.

† This compound exists in two forms, one of which (the yellow) is diamagnetic and the other of which (the blue) is paramagnetic. For other complexes of this type, see Lifschitz, Bos, Dijkema, *Z. anorg. allg. Chem.*, **242**, 97 (1939).

‡ A detailed description of these compounds is in the press: *Jour. Am. Chem. Soc.*

TABLE IV. General Type : $\begin{array}{c} S \diagdown \ N \\ Ni \\ S \diagup \ S \end{array}$

No.	Substance.	$\chi_M \times 10^{-6}$	μ
31	Bis thiosemicarbazide nickel chloride $Ni(NH_2.NH.CS.NH_2)_2Cl_2$ ..	Dia-magnetic	0
32	Bis thiosemicarbazide nickel sulphate $Ni(NH_2.NH.CS.NH_2)_2Cl_2$ ..	Dia-magnetic	0
33	Mono rubeanic acid nickel $(NH : CS.CS : NH)Ni$ ..	Dia-magnetic	0
34	Bis mercaptobenzthiazole nickel $(C_6H_4S.NC : S)_2$ ..	3640	3·0

TABLE V. General Type: $O \searrow Ni \swarrow S$
$S \nearrow \quad \searrow O$

No.	Substance.	$\chi_M \times 10^{-6}$	μ
35	Ethylenebisthioglycollic acid nickel Ni(CH$_2$.S.CH$_2$COO.CH$_2$SCH$_2$COO) ..	2815	2·6

A complex thought to be bis o-hydroxy phenylethyl thioether nickel was paramagnetic. Although the compound contained nearly the correct amount of nickel, there was some doubt about its purity.

TABLE VI. General Type: $S \searrow Ni \swarrow S$
$S \nearrow \quad \searrow S$

No.	Substance.	$\chi_M \times 10^{-6}$	μ
36	Bis xanthic acid nickel† Ni(S.CS.O.C$_2$H$_5$)$_2$	Dia- magnetic	0
37	Potassium nickel dithiooxalate* K$_2$Ni(S.O C : C O.S.)$_2$ . ..	Dia- magnetic	0

† Compounds of nickel formed with N-ethyl dithiocarbamate, N-piperidyl dithiocarbamate are also diamagnetic. Cambi and Szego: *Ber., 64,* 2594 (1931)

and third columns of the tables show the molar susceptibilities ($\chi_M \times 10^{-6}$) at 25° C. and the magnetic moment (μ) of the metal atom in Bohr magnetons respectively. No attempt has been made to include all the results of other investigators but the relevant examples which have been included are indicated by an asterisk. A double asterisk indicates that the results quoted confirm those of a previous investigator.

EXPERIMENTAL AND NOTES TO TABLES I-VI.

Magnetic susceptibilities were measured by the Gouy method and from these, magnetic moments (in Bohr magnetons) were calculated in the usual way. The preparation of the compounds has not been described unless they were new or unless there was any point calling for special mention. Except where there was other evidence for purity, the compounds measured were analysed for nickel content by igniting them to NiO. (See Table VII.)

We are indebted to Dr. F. Lions, who very kindly placed at our disposal substances numbers 2, 8, 25 and 26,‡ and specimens of paonol

‡ Descriptions of these compounds will shortly be published by Dr. F. Lions.

and mercaptobenzthiazole ; to Mr. R. J. Goldacre for his assistance in connection with compounds 31 and 32, and also to Dr. F. Reuter for a specimen of 1 : 8 dinitro naphthalene.

Table I. Ammonium nickel malonate was prepared by adding the calculated amount of malonic acid to a strongly ammoniacal solution of nickel chloride. On allowing the solution to stand, greenish blue prisms of the tetrahydrate separated. This and the related compounds containing ethyl and benzyl malonic acid were prepared several years ago in the hope of obtaining isomers (from the last two). The magnetic data for ammonium nickel malonate make clear the reason for failure to obtain isomers.

Table II. In their description of the two forms of bis α benzoin oxime nickel, Jennings, Sharrat and Wardlaw[6] have stated that both compounds are paramagnetic, without, however, giving any numerical values for susceptibilities. When prepared according to their method and without purification, the buff coloured (α) form is weakly paramagnetic. The susceptibility is too small to be accounted for by two unpaired electron spins in each nickel atom. The weak paramagnetic susceptibility was finally traced to nickel bis benzoin oxime diacetate with which the inner complex was contaminated unless recrystallised from chloroform. Both forms of the internal complex are diamagnetic, and it is theoretically possible that the two are cis and trans isomers arising from square coordination. The practically instantaneous conversion of the reddish (β) form to the α form (in chloroform solution) leads one to suspect that the two may simply be dimorphous forms.

Bis imino paonal nickel was prepared by adding paonol to a strongly ammoniacal solution of nickel chloride as described by Pfeiffer, Golther and Angern.[7] These authors first described the complex so formed as paonol nickel, but in subsequent work they concluded that in strong ammonia solution the ketonic oxygen was in fact replaced by the imino group, a conclusion which is confirmed by the present work. This replacement, incidentally, is an exception to Diehl's[5] general statement " that groups involved in chelation are non-reactive ". This statement is probably true if restricted to groups covalently bound to a metal atom.

Bis o-naphtho quinone dioxime nickel was precipitated as a dark green amorphous powder by the mixing of an alcoholic solution of the oxime with aqueous nickel acetate solution followed by the addition of a few drops of ammonia. Since the method used in its preparation is that which generally leads to a high percentage of the α form, it seems very probable that the oxime used was largely, if not entirely, in this form. At all events the nickel complex is of the type found with anti (α) dioximes, although it has not the usual colour.

Table III. The 1 : 8 naphthalene diamine used in the preparation of compound number 27 was made by reducing a chloroform solution of the corresponding dinitro compound with hydrogen and Raney nickel as described by Ritchie and Albert.[8] Both the 1 : 8 naphthalene diamine and amino guanidine nickel complexes are a bright pink.

TABLE VII.

Substance.	% Ni Found.	Calculated.
Bis o-amino phenol nickel	21·8	21·4
Bis picolinic acid nickel	15·0	15 6
Bis imino paonol nickel	7·3	7·2
Bis 8-hydroxy quinoline nickel	16·7	16·9
Bis benzene azo naphthol nickel	9·7	10 0
Bis semicarbazide nickel sulphate	16·6	16·6
Bis naphthoquinone dioxime nickel	13·3	13·6
Bis 1: 2 naphthalene diamine nickel acetate	13·6	13·7
Bis o-phenylene diamine nickel sulphate	16·6	15·9
Bis 1: 8 naphthalene diamine nickel sulphate ..	12·4	12·6
Bis salicylaldoxime nickel	17·7	17 9
Bis aminoguanidine nickel sulphate	19·0	19·3
Bis mercaptobenzthiazole nickel	14·8	15·1
Bis xanthic acid nickel	22·6	22·4
Mono rubeanic acid nickel	32·6	33 0
Ethylene bisthioglycollic acid nickel	19 5	19·6
Ammonium nickel malonate tetrahydrate	15·9	15·8

DISCUSSION.

Class I.

$$\begin{array}{c} O \diagdown \quad \diagup O \\ Ni \\ O \diagup \quad \diagdown O \end{array}$$
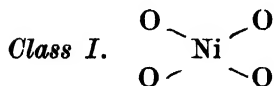
Irrespective of the nature of the functional group in which oxygen occurs, all listed complexes of this class are paramagnetic, a fact which is not surprising in view of the high electro-negativity of oxygen. Although Pauling has not given values for the electro-negativity of the transition elements iron, cobalt and nickel, it is probably not very wide of the mark to assign, by interpolation, a value of about 1·7 for nickel. By using Pauling's relation con-

necting electro-negativity with bond character, rough
values for the amount of ionic character of the different
nickel non-metal bonds can be given as follows :
$Ni-S \sim 15\%$, $Ni-N \sim 35\%$, $Ni-O \sim 60\%$. The magnetic
properties of the members of Class I therefore accord with
what one would expect from electro-negativity con-
siderations.

Class II.
$$\begin{array}{ccc} N & & O \\ & \diagdown \; Ni \; \diagup & \\ O & & N \end{array}$$
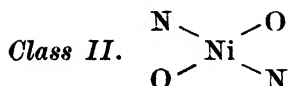
It is among the compounds of this class that there is
the first evidence of the effect of structure on the nature
of bonds between nickel and the non-metallic atoms.   From
Table II it can be seen that Class II contains examples of
both paramagnetic and diamagnetic compounds. In order to
unravel the various factors involved, the compounds will
be further subdivided into two groups, the first of which
includes those compounds in which the oxygen, prior to
linking with nickel, formed part of the hydroxyl group.*
It is then found that with one exception, irrespective of
whether the nitrogen is `N″ (cyclic) or '=NH, —NH₂,
—N=N— or =N—OH the compounds of this sub-group
are diamagnetic and therefore square coordinated.   The
other group comprises the paramagnetic compounds whose
constitution will be considered first.   .

Paramagnetic Complexes of Class II.

Apart from steric factors, the nature of the oxygen
appears to be the factor determining bond type in Class II.
It is significant, for example, that the carbonyl oxygen in
α benzil monoxime leads to a paramagnetic complex,
whereas the hydroxyl group of the closely related α benzoin
oxime leads to the formation of a diamagnetic nickel
complex. Similarly the paramagnetism of bis semi-
carbazide nickelous sulphate appears to be associated with
carbonyl oxygen if the formulation (Fig. 3) suggested by
Smith[9] is accepted.

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* This division is probably an over simplication of the facts of the
case since the possibility of tautomerism in some chelating groups
makes it difficult to say which of two tautomeric forms is actually
involved in complex formation.   In compound 8, for example, it is
considered that the enolic form of the chelate is involved in forming
the metal complex.   It will be necessary to examine more examples
than have yet been studied to clarify this situation.

Paramagnetic compounds are also formed when the oxygen is part of a carboxyl group, as for example in nickel glycine and nickel picolinate.
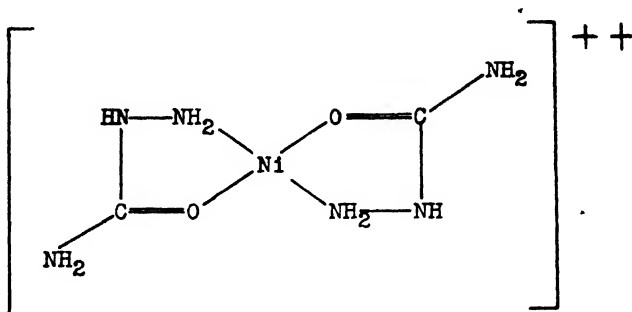
Fig. 3.

Some years ago, in this laboratory, attempts were made to prepare the nickel analogues of cis and trans bis glycine platinum and palladium. The failure which attended repeated efforts can now be understood in the light of the magnetic results, which show that nickel in nickel glycine is not square coordinated. A planar configuration has been found in the argentic and cupric salts of picolinic acid, the crystal structure and optical properties of which have been studied by Cox, Wardlaw and Webster.[10] While the two isomeric forms expected for copper picolinate were isolated, only one form of the nickel salt could be prepared. The magnetic susceptibility of anhydrous nickel picolinate makes the reason for this clear; the compound is paramagnetic and therefore presumably has a tetrahedral* configuration which makes cis-trans isomerism impossible.

One can only speculate as to why oxygen situated as in α benzil monoxime, semicarbazide, glycine and picolinic acid should bring about ionic bonding with nickel. At first sight the effect of structure on the electro-negativity of the oxygen might be held responsible. It is known, for example, that a formal positive charge on an element increases its electro-negativity. However, carbonyl oxygen

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* There is, as yet, not a great deal of evidence to show that paramagnetic complexes of nickel are tetrahedral. One interesting case can however be cited. It is known from crystal structure analysis that in $NiAl_2O_4$ four oxygen atoms are tetrahedrally arranged about nickel. $NiAl_2O_4$ is almost certainly paramagnetic.

has a formal charge of zero, and it is only after forming a third covalent bond that it would assume a formal positive charge. It is more likely that an explanation is to be found in the marked ionic character of the carbon oxygen double bond. This bond (as it occurs in ketones and aldehydes) has a high dipole moment (about $2 \cdot 8 \times 10^{-18}$ e.s.u.) which Pauling[2] interprets to mean that it has some 44% ionic character. The two structures R_2—C=O and R_2—C^+—O^- contribute equally to the normal state of R_2CO. Carbonyl oxygen, the negative end of the dipole, is thus linked to positively charged nickel by an electrostatic bond.

In view of the behaviour of the first eight members (numbers 6 to 13) of Class II the paramagnetism of bis 8-hydroxyquinoline nickel was unexpected. It is suggested that the paramagnetism may arise from steric effects the nature of which will be discussed in more detail in the next section.

Diamagnetic Complexes of Class II.

The effect of electro-negativity on bond character is well illustrated when an oxygen of a Class I complex is substituted by the NH group ; the result of such a substitution is to convert a paramagnetic complex to a diamagnetic one. This has been observed by Tyson and Adams[11] for nickel bis salicylaldehyde and the corresponding aldimine compound, and independently in this laboratory for the complex which is formed when the carbonyl oxygen in p-methoxy o-hydroxy acetophenone is substituted by the imino group.

Colour and Magnetic Properties.

As a rule, the diamagnetic nickel complexes possess colours ranging through different shades of red and brown to yellow. The only exception to the statement that all red complexes of nickel are diamagnetic is afforded by the nickel derivative of ethyl 3 : 3′, 5 : 5′ tetramethyl pyrromethene 4 : 4′ dicarboxylate, which is red by transmitted light and (in the solid state) green by reflected light.[4] The colour of this compound is certainly influenced to a pronounced degree by the colour of the pyrromethene itself. It is nevertheless fairly safe to infer that red complexes are diamagnetic. Most green or greenish blue nickel compounds are paramagnetic. A notable exception to this general statement is to be found in bis salicylal-

doxime nickel, a substance which has been previously reported as diamagnetic.[12] Its colour is so striking that it was thought worthwhile to re-examine it. The compound is undoubtedly diamagnetic. As a matter of interest its absorption spectrum was examined* and the results are plotted in Fig. 4. While there is a rough correlation between colour and magnetic properties, one cannot be

The Absorption Curve of Nickel Salicylaldoxime.
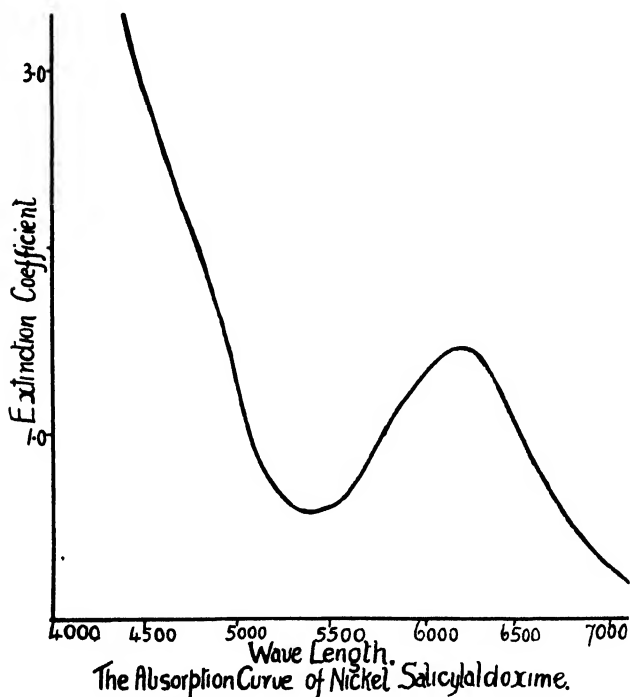
Fig. 4.

certain about magnetic properties from colour alone. Substances like the complexes formed with o-naphthoquinone dioxime and azonaphthol for example are of a rather nondescript colour between a brown and olive green, which is certainly no safe guide as to their magnetic behaviour.

* We are indebted to Dr. R. Lemberg of the Medical Research Institute, Royal North Shore Hospital, for facilities for making the absorption measurements.

Class III.

$$N \diagdown \quad \diagup N$$
$$\quad Ni$$
$$N \diagup \quad \diagdown N$$
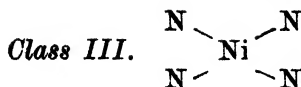
Internal Complexes.

With one exception, to be noted later, internal complexes of Class III are diamagnetic. It was among this class, more particularly among the α (anti)dioxime complexes, that the correlation between configuration and magnetic properties was first established. Feigl[13] has stated that the specific activity of the dioxime group for nickel is lost when the two oxime groups are attached to an unsaturated ring as in o-naphthoquinone dioxime. It is of interest to inquire whether the magnetic character of nickel compounds with dioximes of this class is in any way different from that of bis dimethyl-glyoxime nickel.

In the first place it is doubtful whether it is correct to say that the dioxime grouping is specific for nickel, since palladium readily forms a precipitate with dimethyl-glyoxime in both acid and ammoniacal solution. In any case it seems that the term " specific " is used merely to indicate the formation of an insoluble complex, so that it is not surprising that bis o-naphthoquinone dioxime nickel is, like other α dioxime nickel complexes, diamagnetic. o-Naphthoquinone dioxime may, under a given set of conditions, precipitate many more metals than dimethyl glyoxime,* but the fact that the oxime groups are attached to an unsaturated ring does not significantly alter the character of the Ni-N bonds.

Cationic Complexes of Class III.

Until the present work was begun there appeared to be no record in the literature of diamagnetic compounds of this type, and it was thought that this fact might be associated in some way with the charge of the nickel atom. The present work has, however, brought to light several examples, namely the compounds formed with 1 : 8 naphthalene diamine and amino guanidine. At about the same time, and independently, several examples have been described by Lifschitz and his collaborators. While these diamagnetic compounds are undoubtedly square coordinated, it is difficult to be sure of the constitution of

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* It has been stated that o-naphthoquinone dioxime functions as a dibasic acid towards many metals. While this is true for cobalt, it does not hold for nickel.

paramagnetic compounds like those formed with o-phenylene diamine and 1 : 2 naphthalene diamine since magnetic measurements do not permit a distinction to be drawn between ionic, sp^3 and d^2sp^3 bonding. However, a tentative explanation in terms of steric effects is suggested to account for the difference in behaviour of the nickel compounds with 1 : 2 and 1 : 8 naphthalene diamine, for example.

The angular dependence of the strength of a dsp^2 bond (in the plane of the bonds) is given by the following diagram (Fig. 5), which is a plot of the function :

$$f(\varphi) = \tfrac{1}{2} + 1\cdot221 \ \cos \ \varphi + 0\cdot965 \ \cos \ 2\varphi$$
$$f(\varphi) = \text{strength of bond.}$$
$$\varphi = \text{angle between bond direction and line of reference.}$$
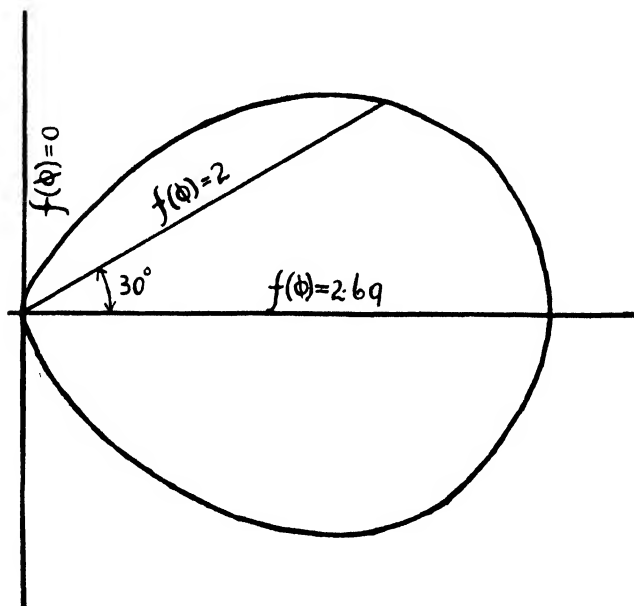
Fig. 5.

From this it can be seen that (1) the bond strength is a maximum ($2\cdot69$ units) when $\varphi = 0$; (2) the bond strength falls to a value of 2 units for $\varphi = 30°$. Now the best tetrahedral (sp^3) bond also has a strength of 2 units. If, through the operation of some steric factor, an atom which

normally forms four square bonds has its bond directions
deflected by more than 30° from their natural directions,*
it seems reasonable to assume that sp³ or ionic bonds will
be formed in preference to dsp² bonds.

Magnetic susceptibility measurements show that ionic
or sp³ bonding does occur in the nickel derivative of ethyl
3 : 3′, 5 :′5′ tetramethyl pyrromethene 4 : 4 dicarboxylate.
By assuming that the methyl groups remain in the plane
of the pyrrole rings, and that all the bending occurs in the
Ni-N bonds, calculation shows that distortion amounts to
approximately 40° for each bond.   It is therefore not
surprising to find that while all other inner complexes with
four Ni-N bonds are diamagnetic, the pyrromethene
complex is paramagnetic.

The bond angle distortion which occurs in the pyrro-
methene complex arises from clashing of α methyl groups
attached to the chelating nitrogen atoms.   It is suggested
that in o-phenylene diamine nickelous sulphate (and the
corresponding 1 : 2 naphthalene diamine salt) steric effects
come into play between the chelating nitrogen atoms
themselves.

Fig. 6 shows the bond lengths and relative positions of
the atoms in the o-phenylene diamine nickel ion.   The
C-N bonds are assumed to come off the rings symmetrically,
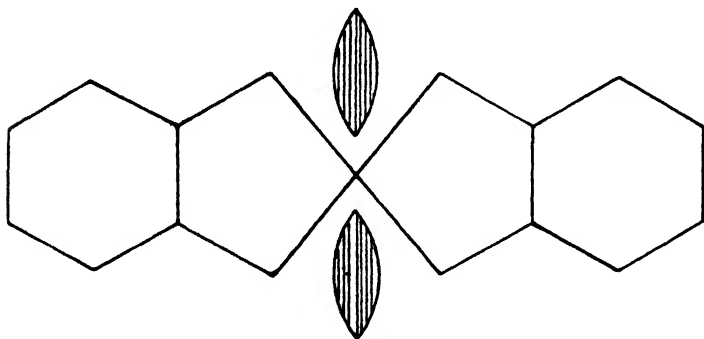
Fig. 6.

Ortho phenylene diamine nickelous ion, showing clashing of
nitrogen atoms.

* It must be assumed that the horizontal axis in the above figure is
one of rotational symmetry.

as they do in all aromatic compounds which have been investigated by X-ray crystal analysis. By using the relevant interatomic distances and assuming that the Ni-N bonds are covalent (and $1 \cdot 9$ A.U. in length) the bond angles at the nickel atom prove to be approximately $85°$ and $100°$ for 1 : 8 naphthalene diamine and orthophenylenediamine respectively. The overlapping of the atoms (indicated by shading) accompanying the larger bond angle at nickel, suggests that a more stable configuration may be attained by a twisting of the two halves of the molecule relative to one another. Certain difficulties arise in connection with this suggestion. It is known, for example, that in carbon tetrachloride the chlorine atoms approach one another more closely than the sum of their van der Waals radii. This is true even of the chlorine atoms in methylene chloride and chloroform. Four nitrogen atoms covalently bound to nickel and located in the same plane in such a way that the angles are exactly $90°$ must also approach one another more closely than their sum of the van der Waals radii. There must, however, be some limit to this closer approach of non-bonded nitrogen atoms. While it is impossible to say just how large a bond angle at nickel could be tolerated without distortion of the bonds from their coplanar configurations, it is conceivable that in some chelate rings this limiting angle may well be exceeded.

Before leaving the cationic complexes of Class III reference must be made to compound 24, bis 8-amino quinoline nickel nitrate. Considerable doubt has recently been thrown on the work of Reihlen and Huhn,[14] in which they claimed to have resolved platinous, palladous and nickelous compounds of 2-amino methyl 3-methyl 4-ethyl quinoline. Susceptibility measurements show that the 8-amino quinoline complex is paramagnetic. It is very probable that Reihlen and Huhn's closely related nickel complex is also paramagnetic and therefore tetrahedral. With these considerations in mind the α bromo π camphor sulphonate of 8-amino-quinoline nickelous ion was prepared. Fractional crystallisation from water, chloroform and alcoholic chloroform solutions failed to produce any evidence of optical activity in the nickel complex. This negative result may possibly be due to causes other than lack of optical asymmetry, and like most negative results can be given little significance.

Class IV. $\overset{N}{\underset{S}{\diagdown}} Ni \overset{S}{\underset{N}{\diagup}}$
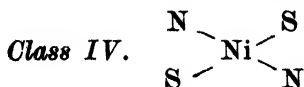
Few representatives of the remaining classes have been measured; indeed few compounds of these classes have been described in the literature, and among even these there are compounds to which it is difficult to assign a structure. Thus bis mercaptobenzthiazole nickel might equally well be assigned to Class VI or IV. It is provisionally placed in IV.

The metal complexes of thiosemicarbazide have however been studied in great detail by Jensen,[15] and on the basis of his evidence for the structure of bis-thiosemicarbazide nickel salts, they have been assigned to class IV. These compounds are diamagnetic and this is what one would anticipate from the position of sulphur and nitrogen in the electro-negativity series. Their diamagnetism also shows that cis-trans isomerism might be expected to occur. Such was actually found to be the case by Jensen in his later investigation of bis thiosemicarbazide nickel chloride.

In the rubeanic acid nickel complex there is only one molecule of the acid to each nickel atom. The possibility of nickel being only bicovalent is ruled out by the observed diamagnetic susceptibility. A plausible structure involving polymerisation is indicated below.

Fig. 7.

Class V. $\overset{S}{\underset{O}{\diagdown}} Ni \overset{O}{\underset{S}{\diagup}}$
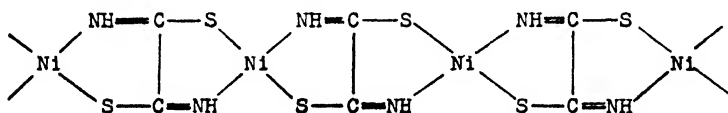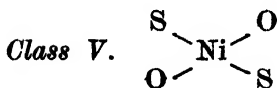
Only one compound of this class has so far been investigated, and this proves to be ionic. The fact that some complexes of Class II $\left(\overset{N}{\underset{O}{\diagdown}} Ni \overset{O}{\underset{N}{\diagup}} \right)$ are diamagnetic, and also, that sulphur is less electro-negative than nitrogen, lead to the expectation that diamagnetic representatives of this class might well be found. Attempts to synthesize examples were however unsuccessful.

The ionic character of ethylene bis thioglycollic acid nickel is attributed to the fact that the two oxygens of the quadridentate group are both part of carboxyl groups.

Class VI. $\underset{S}{\overset{S}{\diagdown}} Ni \underset{S}{\overset{S}{\diagup}}$
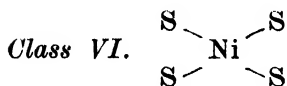
As far as electro-negativity considerations are concerned this class (VI) represents the most favourable conditions for forming covalent bonds. The one compound measured, namely bis xanthic acid nickel, bears out this conclusion. Other representatives of this class investigated by Cambi are magnetically similar to bis xanthic acid nickel. It should be pointed out that with xanthic acid there are two alternative ways of forming four-membered chelate rings. The one involving oxygen to which an ethyl group is already attached is considered very improbable in view of Feigl's work on the coordinating capacity of the two methyl ethers of salicylaldoxime. Hence it is presumed that coordination occurs through two sulphur atoms.

SUMMARY.

From a survey of the magnetic properties of nickel complexes it is shown that while the electro-negativity of the atoms attached to nickel plays an important role in determining the character of the nickel-non-metal bond, other factors may be significant. These include (1) effects due to structure, such as the nature of the functional group in which the atom (oxygen, for example) bonded to nickel occurs ; (2) certain steric effects.

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MAGNETIC STUDIES OF COORDINATION COMPOUNDS.

PART IV. SQUARE COORDINATED COBALTOUS COMPOUNDS.

By D. P. MELLOR, M.Sc., and D. P. CRAIG.

In order to explain the existence of certain pairs of cobaltous compounds such as α and $\beta[Co(NH_3)_2Cl_2]$ and the corresponding pyridine compounds, it has been assumed that the two ammonia (or pyridine) molecules and the two chlorine atoms are arranged about cobalt in a coplanar configuration in such a way as to form cis and trans isomers.[1] In a previous paper[2] it has been pointed out that the magnetic properties of these compounds do not support this assumption. The question arises then whether cobalt (Co^{II}) is ever square coordinated.

In a recent investigation of cobalt (chiefly cobaltic) complexes, Cambi and Malatesta[3] report that cobaltous bis α benzildioxime has a moment of $2 \cdot 04$ Bohr magnetons. These authors interpreted this to mean that the cobaltous atom has one unpaired electron. One unpaired electron spin is just that predicted by Pauling for a square coordinated cobaltous atom. Hence it may be concluded that cobaltous bis α benzildioxime has a planar structure and that the same kind of structure may well characterise other complexes. This paper describes the results of susceptibility measurements made on a number of cobaltous compounds, mainly of the internal complex type, with a view to finding out to what extent cobalt resembles nickel in its tendency to form square coordinated complexes. The results are summarised in Tables I-VII. The compounds have been classified as in Part III, and, as before, the second and third columns of the tables show molar susceptibilities ($\chi_M \times 10^{-6}$) at 25° C. and the magnetic moment (μ) of the metal atom in Bohr magnetons respectively.

TABLE I. General Type:
$$\begin{matrix} O & & O \\ & Co & \\ O & & O \end{matrix}$$

No.	Substance.	$\chi_M \times 10^{-6}$	μ
1	Bis guaiacol cobalt Co(–O–C$_6$H$_4$–CH$_2$O–)$_2$	8400	4·5
2	Bis salicylaldehyde cobalt* Co(–O–C$_6$H$_4$–CHO–)$_2$	8180	4·5

* Tyson and Adams, *Journ. Am. Chem. Soc.*, 1940, *62*, 1228.

TABLE II. General Type:
$$\begin{matrix} O & & N \\ & Co & \\ N & & O \end{matrix}$$

No.	Substance.	$\chi_M \times 10^{-6}$	μ
3	Bis salicylaldehyde ethylene diamine cobalt Co(O–C$_6$H$_4$–CH : en : CH–C$_6$H$_4$–O) ..	1120	1 76
4	Bis salicylaldoxime cobalt Co(O–C$_6$H$_4$–CH : NO)$_2$	2678	2·6
5	Bis o-amino phenol cobalt Co(O–C$_6$H$_4$–NH$_2$)$_2$	2650	2·5
6	Mono benzene azo naphthol cobalt Co(–O–C$_{10}$H$_4$–N : N–Ph)	10950	5·0
7	Tris α benzoin oxime cobalt Co(Ph–C : NO.CHOH–Ph)$_3$	6410	4·0
8	Bis semicarbazide cobaltous sulphate Co(–O–NH$_2$–C : N–NH$_2$)$_2$SO$_4$	6680	4·2

TABLE III. General Type:
$$\begin{matrix} N & & N \\ & Co & \\ N & & N \end{matrix}$$

No.	Substance.	$\chi_M \times 10^{-6}$	μ
9	Bis dimethyl glyoxime cobalt Co(CH$_3$.C.NOH.NO.CCH$_3$)$_2$	2835	2·6
10	Bis benzyl methyl glyoxime cobalt Co(Ph–C–NOH.NO.CCH$_3$)$_2$	3205	2·87
11	Bis α benzildioxime cobalt Co(Ph–C–NOH.NO–C–Ph)$_2$	1770	2·16
12	Bis pyridylbenziminazole cobaltous thiocyanate† [Co(N$_3$C$_{12}$H$_9$)$_2$] [CNS]$_2$	9125	4 7
13	Mono naphthoquinone dioxime cobalt Co(C$_{10}$H$_4$.NO.NO)	10660	5·0
14	Bis pyridino bis diazoaminobenzene cobalt Co(Ph–N : NH.Ph)$_2$Py$_2$	8025	4·4
15	Bis 1 : 2 naphthalene diamine cobaltous acetate Co(C$_{10}$H$_4$.NH$_2$.NH$_2$)$_2$(OAc)$_2$	9750	4·7

† We are indebted to Dr. F. Lions for a specimen of this substance, which along with related compounds will shortly be described by him.

TABLE IV. General Type: $\begin{array}{cc} S\diagdown & \diagup N \\ & Co \\ N\diagup & \diagdown S \end{array}$

No.	Substance.	$\chi_M \times 10^{-6}$	μ
16	Bis rubeanic acid cobalt $Co(NH:CS\text{-}SC:NH)_2$	3450	2 9
17	Bis thiosemicarbazide cobalt $Co(NH_2.CS.NH.NH_2)_2$	2450	2·3

TABLE V. General Type: $\begin{array}{cc} S\diagdown & \diagup O \\ & Co \\ O\diagup & \diagdown S \end{array}$

No.	Substance.	$\chi_M \times 10^{-6}$	μ
18	Ethylene bisthioglycollic acid cobalt $Co(OOC\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}COO)$	9295	4·7

TABLE VI. General Type: $\begin{array}{cc} S\diagdown & \diagup S \\ & Co \\ S\diagup & \diagdown S \end{array}$

No.	Substance.	$\chi_M \times 10^{-6}$	μ
19	Bis xanthic acid cobalt $Co(\text{-}S\text{-}CS\text{-}O\text{-}C_2H_5)_2$	2514	2·4

TABLE VII. Additional Complexes.

No.	Substance.	$\chi_M \times 10^{-6}$	μ
20	Bis p-toluidine cobaltous chloride* $Co(CH_3\text{-}C_6H_4\text{-}NH_2)_2Cl_2$	9760	4·75
21	Bis anilino cobaltous chloride* . $Co(Ph.NH_2)_2Cl_2$ . ..	11480	5 25

* The authors are indebted to Mr. N. Hills for specimens of these substances.

EXPERIMENTAL AND NOTES ON THE TABLES.

Magnetic susceptibilities were measured by the Gouy method and magnetic moments were calculated in the usual way.

Table I. Bis guaiacol cobalt. Cobaltous acetate (2·1 g.) in 50% aqueous alcohol solution was added to guaiacol dissolved in alcohol and two drops of ammonia added to the mixture. The complex separated as a pale blue amorphous precipitate. No corresponding nickel complex could be obtained under these conditions.

Table II. Bis salicylaldimine cobalt. All attempts to prepare pure specimens of this compound failed. Prolonged contact of bis salicylaldehyde cobalt with concentrated ammonia solution did, however, bring about a partial conversion to the aldimine complex. The solid separated after this treatment contained $7 \cdot 3\%$ nitrogen (bis salicylaldimine cobalt requires $19 \cdot 7\%$) and behaved as though cobalt had a moment of $3 \cdot 3$ Bohr magnetons. These observations show that a partial conversion to the aldimine compound was effected. Owing to the impurity of the compound the magnetic data for this substance have not been included in Table II.

Bis salicylaldehyde ethylenediamine cobalt. The quadridentate chelate was prepared by condensing one molecule of ethylenediamine with two molecules of salicylaldehyde in alcohol solution. On adding an alcohol solution of bis salicylaldehyde ethylenediamine to cobaltous acetate the complex separated as a brown precipitate.

Table III. Bis diazoaminobenzene cobalt. All attempts to prepare pure specimens of this complex were unsuccessful. The method tried was to make first the bis pyridine bis diazoaminobenzene complex, which readily formed, and then to remove the pyridine, as was done in preparing the corresponding nickel derivatives. Complete removal of the pyridine was never effected without also decomposing much of the diazoaminobenzene cobalt.

Table VI. Bis xanthic acid cobalt. This was prepared as a brown powder by simply adding an alcohol solution of the acid to cobaltous acetate solution.

Analyses for Cobalt.

All substances measured were analysed for cobalt content by carefully decomposing them with concentrated sulphuric acid, and weighing the cobalt as anhydrous cobalt sulphate. The results are summarised in the table on p. 499.

DISCUSSION.

From Tables I-VII it can be seen that many cobaltous complexes have moments lying between $1 \cdot 73$ and $2 \cdot 88$ Bohr magnetons. The difference between the observed values and that expected for one electron spin ($1 \cdot 73$ Bohr magnetons) is attributed to orbital contribution, which, in general, is rather large but comparable in magnitude with that found among ionic cobaltous complexes. The deviation of the observed moments from the theoretical value cannot be attributed to the existence of resonance hybrids with different numbers of unpaired electrons since this would violate the conditions for resonance which can be stated as follows : " In order for continuous transition

Substance.	% Co Found.	% Co Calculated.
Bis guaiacol cobalt	19 0	19·3
Bis salicylaldehyde cobalt..	19 4	19·6
Benzene azo naphthol cobalt	19·3	18·1
Bis salicylaldehyde en cobalt	18 6	18·2
Tris α benzil monoxime cobalt	7·7	8·0
Bis salicylaldimine cobalt	7·3	19·7
Bis salicylaldoxime cobalt	17·3	17·7
Tris α benzoin oxime cobalt	8·5	8·1
Bis o-amino phenol cobalt	21 1	21·4
Tris α nitroso β naphthol cobalt	10·1	10 25
Bis semicarbazide cobaltous sulphate	16 5	16 6
Bis dimethyl glyoxime cobalt	20 0	20 4
Bis benzyl methyl glyoxime cobalt	14·7	14 4
Bis α benzildioxime cobalt	10 7	10 93
Naphthoquinone dioxime cobalt	26·2	26 4
Bis 1 : 2 naph. diamine cobaltous acetate .. .	13 9	13 7
Bis rubeanic acid cobalt	19 8	19 75
Bis thiosemicarbazide cobalt	23 7	24 7
Bis mercaptobenzthiazole cobalt	15·1	15 1
Ethylene bisthioglycollic acid cobalt	21·9	22·4
Bis xanthic acid cobalt	20 0	19·6

to be possible between two extreme bond types the conditions for resonance between the corresponding structures must be satisfied. The most important of these conditions is that the two structures must involve the same numbers of unpaired electrons."[4]

The tables show that most of the organic compounds which produce square complexes with nickel also do so with cobalt (Co[II]). The few exceptions include amino guanidine, α benzoin oxime and benzene azo β naphthol. Hence most of the discussion given for nickel in our preceding paper (Part III) is applicable to cobalt. While there is much similarity between Ni[II] and Co[II] in regard to their tendency to form square complexes, the same tendency is not shown by Fe[II] and Mn[II]. For neither of these last two metals has any instance of square coordination, even

under the most favourable circumstances,* been reported. It is perhaps worth noting that all square coordinated metal atoms contain either zero unpaired electrons (Ni^{II}, Pt^{II}, Pd^{II}, Au^{III}) or one unpaired electron (Cu^{II}, Ag^{II}, Co^{II}, etc.). Square coordination has not been found for any metal which (if square) would be expected to contain two (Fe^{II}, Co^{III}) or more unpaired electrons (Mn^{II}, Fe^{III}, etc.).

The square covalent complexes of Co^{II} are surprisingly stable in contact with water, especially as compared with the octahedral covalent complexes of Co^{II}. Two reasons may be advanced for this difference in behaviour. The insolubility of the complexes is no doubt partly responsible.† Another contributing factor is to be found in the electron configurations of square and octahedral Co^{II}, which are represented in Fig. I (outer shells only are shown). The bond-forming orbitals are shown in rectangular enclosures.
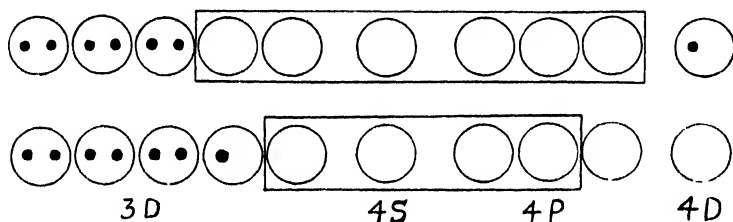
Fig. 1.

It can be seen that when octahedral bonds are formed with the use of two 3d orbitals, only three 3d orbitals are left to accommodate the remaining seven electrons.‡

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* As in the phthalocyanine and protoporphyrin complexes. Co^{II} is undoubtedly square coordinated in these complexes.

† In this connection compare the difference in behaviour between chromous acetate and chromous chloride in contact with water.

‡ It can be seen from Fig. 1 that octahedral Co^{II} complexes should also have one unpaired electron. This has been verified for K$_2$Ca[Co^{II}(No$_2$)$_6$][5], which has a moment of 1·9 Bohr magnetons. A moment of the same order is expected for K$_4$[Co^{II}(CN)$_6$], but curiously enough this substance is diamagnetic both in the solid state[6] and in solution. Experiments (with R. J. Goldacre) in this laboratory which have been confined to solutions of K$_4$Co^{II}(CN)$_6$ confirm the observations made on the solid. One possible way of explaining this apparent anomaly is to postulate a metal-metal bond arising from polymerisation. The [Co(CN)$_6$]$\equiv$ ion cannot polymerise if Co^{II} is to retain its coordination number of six. Electrometric investigations of Glasstone and Speakman[7] have shown that the complex ion in solution contains five CN groups per cobalt atom, [Co(CN)$_5$]$\equiv$. The ion is very probably [Co$_2$(CN)$_{10}$] with the structure : [(CN)$_5$Co·Co(CN)$_5$], the metal-metal bond of which results in the pairing of the odd electron on each cobalt atom.

" The seventh electron must accordingly occupy an outer unstable orbital causing the complex to be unstable."[4] On the other hand when square bonds are formed the odd electron can be accommodated in one of the 3d orbitals without introducing any instability.

As in the case of nickel, there is a rough correlation between the colour and magnetic properties of cobaltous compounds. The covalent complexes are generally some shade of brown, while the ionic complexes vary in colour from pink and mauve to blue. The correlation is not sufficiently complete to enable a classification to be made on the basis of colour alone.

One of the objects of undertaking this survey was to use magnetic data as a guide in the search for cis-trans isomerism among the planar cobaltous complexes. Although it was theoretically possible for many of the compounds measured, no instance of such isomerism was brought to light. The search is being continued.

SUMMARY.

Magnetic susceptibility measurements show that Co^{II} resembles Ni^{II} in its ability to form square coordinated complexes. Some of the characteristics of square covalent cobaltous compounds are briefly described.

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PERMIAN BRYOZOA OF EASTERN AUSTRALIA.

PART II. NEW SPECIES FROM THE UPPER MARINE SERIES OF NEW SOUTH WALES.

By JOAN M. CROCKFORD, B.Sc.

(With Plates XX and XXI and three Text-figures.)

INTRODUCTION.

The species of Bryozoa here described belong to the genera *Batostomella* Ulrich, *Fenestrellina* d'Orbigny, *Polypora* McCoy, *Ptilopora* McCoy, and *Rhombopora* Meek. The distribution of the species described and their relative measurements are shown in the accompanying tables.

TABLE 1.—*Distribution of Species.*

Species.	Allandale.	Branxton.	Belford.	Mulbring.	Ulladulla.	Shoalhaven Heads.	Glenorchy.	Marlborough
Batostomella cylindrica					x			
Fenestrellina bituberculata				x				
Fenestrellina altacarinata		x	x		x			
Fenestrellina quinquecella					x			x
Fenestrellina granulifera		x	x					
Fenestrellina canthariformis			x	x				
Polypora dichotoma ..					x			
Polypora triseriata ..					x			
Polypora multinodata			x					
Polypora magnafenestrata	x	x	x	x	x		x	
Polypora linea		x		x				
Ptilopora carinata ..						x		
Rhombopora filiformis ..					x			

Table 2.—*Measurements of Species of Fenestrellina and Polypora.*

Species.	Locality.	Branches.		Fenestrules.		Width of Dissepiments.	Zoœcia.			Nodes.	Carina.
		No. in 10 mm.	Width.	No. in 10 mm.	Length.		No. of Rows.	No. in 10 mm.	No. per Fenestrule.		
			mm. 0·67-0·77		mm.	mm.					
Fenestrellina bituberculata.	Mulbring.	9-12	0·67-0·77	5-5·5	1·1-1·7	0·2-0·55	2	23	4	In two rows, 8 to a fenestrule.	Poorly developed
Fenestrellina alta-carinata.	Belford.	12	0·4-0·7	6	1·08-1·67	0·2-0·55	2	24	4-5	Not developed.	Very high.
Fenestrellina quinque-cella.	Ulladulla.	14-15	0·34-0·56	7-8	0·77-1·08	0·32-0·56	2	32	5 (rarely 4)	Large, 0·3-0·65 mm. apart.	Slight.
Fenestrellina granulifera.	Branxton.	10-11	0·4-0·47	7-7·5	0·94-1·2	0·23-0·47	2	24	3 (less often 4)	Large, about 0·37 mm. apart.	Not high.
Fenestrellina canhariformis	Belford.	20-24	0·18-0·29	16-17	0·88-0·58	0·08-0·19	2	About 34	2	Very high, about 0·24 mm. apart.	Slight.
Polypora dichotoma ..	Ulladulla.	7-8	0·9-1·2	5-5·5	0·85-1·1	0·6-0·94	4	23	4-5	Small, poorly developed.	—
Polypora triseriata ..	Ulladulla.	10	0·8	5	1·44-1·66	0·38-0·48	3	20	4	Small.	—
Polypora multinodata	Belford.	7-9	0·7-1·1	4-4·5	1·31-2·52	0·34-0·89	4	19	4	Strongly developed.	—
Polypora magnafenes-trata.	Branxton.	5-7	0·8-1·4	1·5-3	1·0-7·5	0·32-0·56	4-5	18	5-11	Rarely developed.	—
Polypora linea ..	Mulbring.	6-7	1·2	2·5-3	2·9-3·8	0·27-0·32	5	About 20	6-9	Large.	—

The species are mostly restricted to the Upper Marine Series of New South Wales, but one species, *Polypora magnafenestrata*, extends into the Lower Marine, and two species, *Fenestrellina quinquecella* and *Polypora magnafenestrata*, occur also in the Permo-Carboniferous of Tasmania.

DESCRIPTION OF SPECIES.

Family BATOSTOMELLIDÆ Ulrich.

Genus Batostomella Ulrich.

Batostomella cylindrica n.sp.

(Pl. XX, fig. 1 : text-figure 1.)

Holotype : F.24005, Australian Museum Collection, from the Ulladulla Mudstones, North Head, Ulladulla.

Ramose, branches 2-2·7 mm. in diameter; mesopores and acanthopores well developed; mature region one-third of the radius.

The zoarium is ramose and divides dichotomously at intervals of more than 2 cm. ; the branches are of the same diameter as the original stem, and are circular in cross section, from 2·0 to 2·7 mm. in diameter. The apertures are irregularly placed and are oval with the long axis parallel to the length of the zoarium, being from 0·3 to 0·4 mm. in length, and from 0·2 to 0·3 mm. in width. Acanthopores are usually in one row on the interspaces between the zoœcia, with about eight surrounding each aperture, and project above the surface for about 0·2 mm. Mesopores are irregularly developed in the mature region ; at the surface of the zoarium they are round or oval, from 0·1 to 0·25 mm. in diameter. Small monticules are infrequently developed ; they do not differ in zoœcial characters from the rest of the surface ; mesopores and acanthopores may be more numerous along one side of the branch. In transverse section the zoœcial tubes are irregularly angular in outline in the centre of the zoarium. The walls are very much thickened in the outer third of the radius ; in the central part they are very thin ; the tubes bend rather sharply from the immature to the mature region. Diaphragms are rarely developed in the mature region.

Remarks : This species is distinguished from *Batostomella spinigera* Bassler (Permian, Thie, Rotti) by the relative

width of the mature zone, and by the angle at which the zocecia bend to the mature zone.

Family FENESTRELLINIDÆ Bassler.

In several of the species of *Fenestrellina* and *Polypora* here described small rounded cells are developed on the celluliferous surface ; these are best shown when the outer granular layer is slightly worn and may normally have been covered by it ; the upper surface sometimes shows a small perforation ; they easily break away and leave a hemispherical scar, and were probably originally hollow ; they are fairly frequently developed in these species. Ulrich (1890, p. 557) has described similar cells in *Semicoscinium rhombicum* Ulrich.
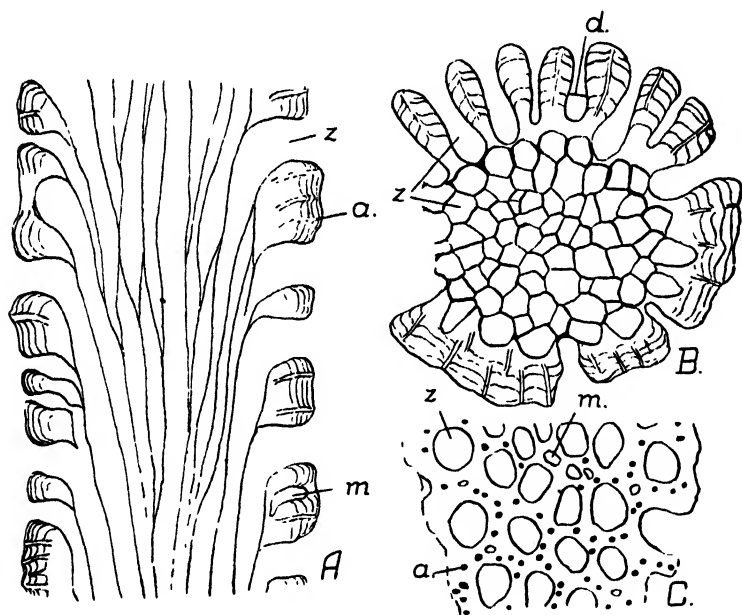
Text-figure 1. *Batostomella cylindrica.*

A. Vertical section. B. Transverse section. C. Tangential section (*camera lucida* diagrams).   ×20.

z, Zocecial tubes ; a, acanthopores ; m, mesopores ; d, diaphragm.

(A and B, specimen 1438, Sydney University Collection ; C, specimen F.24001, Australian Museum Collection.)

Genus Fenestrellina d'Orbigny.
Fenestrellina bituberculata n.sp.
(Text-figure 2B.)

Holotype : 1424, Sydney University Collection, from the Fenestella Shales, Por. 126, Parish of Mulbring.

Fenestrellina with a double row of nodes on the carina and four apertures in the length of one fenestrule ; about five fenestrules and nine to twelve branches in 10 mm.

The form of the colony is not known ; the specimens are rather flat expansions up to three inches in length. There are 9 to 12 branches horizontally, and 5 to 5·5 fenestrules vertically in 10 mm. The branches are fairly straight, usually from 0·67 to 0·77 mm. in width ; they are sharply convex in the celluliferous surface ; the carina is very poorly defined and is formed only by the junction of the sides of the branches ; generally a double row of well marked nodes occurs on the carina ; the spacing of the nodes is very irregular, up to eight occurring in the length of one fenestrule. Small, rounded surface cells are occasionally developed. The zoœcial apertures are placed on the sloping sides of the branches and project slightly into the fenestrules ; the area about each zoœcial aperture is raised slightly above the level of the branch. There are usually four apertures in the length of each fenestrule, one of these may be placed opposite the end of a dissepiment. The apertures are circular, about 0·19 mm. in diameter, and show slight peristomes ; they are separated by at least their own diameter, the distance between the centres of successive apertures being 0·35 to 0·59 mm. ; there are twenty-three apertures in 10 mm. The fenestrules are rather oval in outline, and are usually from 1·1 to 1·7 mm. in length and about 0·65 mm. in width, although they are occasionally very much shorter or narrower. The dissepiments are from 0·21 to 0·55 mm. in width ; the total length of one fenestrule and one dissepiment is from 1·65 to 1·93 mm. The dissepiments are flat to slightly rounded on the celluliferous surface ; the reverse surface is not shown. 'Bifurcation occurs at intervals generally of 2 cm. or more ; increase to three, then four, rows of zoœcia may occur a considerable distance before bifurcation.

Remarks : This species resembles *Fenestrellina kukœnsis* (Bassler) from the Permian of Timor, but is separated from this and other species showing a double row of nodes on the carina by its larger size.
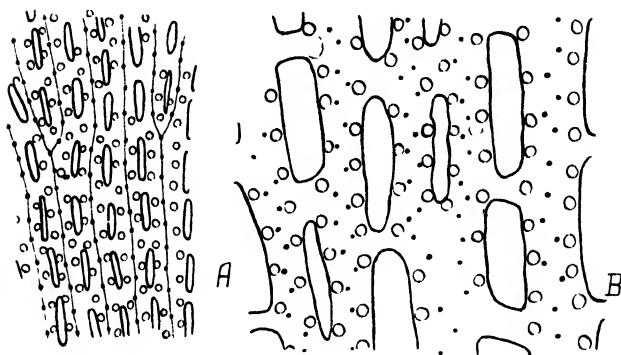
Text-figure 2.

A. *Fenestrellina canthariformis.* Celluliferous surface of the holotype.
×10. B. *Fenestrellina bituberculata.* Celluliferous surface of
the holotype.   ×10. (*Camera lucida* diagrams.)

Fenestrellina altacarinata n.sp.

(Pl. XXI, fig. 6.)

Holotype : 1421, Sydney University Collection, from the
Fenestella Shales, Por. 15, Parish of Belford.

*Fenestrellina with a very high carina, and oval fenestrules,
with four zoœcia to a fenestrule.*

The form of the zoarium is not known. There are 12
branches horizontally, and 6 fenestrules vertically in
10 mm. The fenestrules are oval in outline ; the branches
have a slightly flexuous appearance, accentuated by the
wavy, very high carina ; the carina is not quite so high
opposite the dissepiments and before branching. The
zoœcial apertures are placed on the slightly sloping sides
of the branches. Nodes are not developed. The zoœcial
apertures are circular, $0 \cdot 16$ mm. in diameter ; there are
four (rarely five) zoœcia to a fenestrule (two of these may
be placed opposite a dissepiment), the distance between
the centres of successive apertures being from $0 \cdot 38$ to
$0 \cdot 49$ mm. The fenestrules are $1 \cdot 06$ to $1 \cdot 67$ mm. (average
$1 \cdot 23$ mm.) in length, and $0 \cdot 32$ to $0 \cdot 66$ mm. (average
$0 \cdot 48$ mm.) in width. The dissepiments are $0 \cdot 41$ mm.
($0 \cdot 2$ mm. to $0 \cdot 55$ mm.) and the branches $0 \cdot 53$ mm. ($0 \cdot 4$
mm. to $0 \cdot 7$ mm.) in width. On the reverse surface the
branches are slightly thicker than the dissepiments.
Bifurcation occurs at intervals of more than 7 mm. :
increase to three rows of zoœcia occurs within one fenestrule
before bifurcation.

Fenestrellina quinquecella n.sp.

(Pl. XXI, fig. 3.)

Holotype : 1422, Sydney University Collection, from the Ulladulla Mudstones, Warden Head, Ulladulla.

Fenestrellina with five (less often four) zoœcia to a fenestrule; slight carina with large nodes.

The form of the colony is not shown ; there are 14 to 15 branches horizontally and 7 to 8 fenestrules vertically in 10 mm. The branches are from 0·34 to 0·56 mm. wide, and the sides slope steeply towards the fenestrules ; the carina is formed chiefly by the junction of the sides of the branches and is not high. Nodes are irregularly placed, 0·3 to 0·65 mm. apart. There are usually four (rarely three) zoœcia in the length of one fenestrule, with an extra one opposite each dissepiment. The apertures are circular, 0·14 to 0·18 mm. in diameter, with well marked peristomes, and do not project into the fenestrules ; they are separated by a length about equal to their diameter, the distance between the centres of successive apertures being 0·27 mm. to 0·35 mm. ; there are about thirty-two apertures in 10 mm. The fenestrules are sub-rectangular, 0·77 to 1·08 mm. long, and 0·27 to 0·45 mm. wide ; the dissepiments are relatively very broad—0·32 to 0·56 mm. ; and the total length of a fenestrule and a dissepiment is from 1·15 to 1·4 mm. The dissepiments are evenly rounded on the celluliferous surface. On the reverse surface the dissepiments are about as thick as the branches ; each branch is steeply convex and the ridge formed by the junction of these sides is rather sinuous, so that the dissepiments appear very short and the fenestrules hexagonal. The outermost layer on this surface is finely granular, and may be fairly thick ; the next layer shows the striæ on the branches swinging across the dissepiments and repeats the indistinct division to branches and dissepiments seen in the outer layer ; beneath this about eight straight longitudinal striæ occur on the branches. Both striated layers show fine perforations. Bifurcation occurs generally at intervals of 3 cm. or more ; increase to three rows of zoœcia occurs within four fenestrules before bifurcation ; coalescence of two branches after bifurcation occurs in one or two places. There is generally a short length of non-celluliferous material separating the two branches.

Remarks : From *Fenestrellina exserta* (Laseron), which shows the same number of zoœcia to a fenestrule, this species is distinguished by its smaller size, and from *F. granulifera*, which shows similar measurements, it is distinguished by the number of zoœcia to a fenestrule. *F. altacarinata* has a very much higher carina and more widely spaced apertures, and nodes are not developed.

Fenestrellina granulifera n.sp.

(Pl. XXI, fig. 4.)

Protoretepora or *Phyllopora* sp. Laseron, 1918, *Jour. Roy. Soc. N. S. Wales, 52,* pl. III, fig. 1.

Holotype : 1427, Sydney University Collection, from the upper part of the Fenestella Shales, railway cutting 1 mile west of Branxton.

Fenestrellina with three to four zoœcia in the length of one fenestrule and one dissepiment ; slight carina with strongly-developed nodes ; reverse surface coarsely granular.

The form of the colony is not known ; there are 10 to 11 branches horizontally, and 7 to 7·5 fenestrules vertically in 10 mm. The branches are straight, 0·4 to 0·47 mm. in width, and show a median carina, not very high but with strong nodes about 0·37 mm. apart. The zoœcial apertures are placed on the sloping sides of the branches ; the apertures are circular, 0·16 to 0·18 mm. in diameter, and are frequently closed by a centrally-perforated calcareous plate. There are three to four apertures in the length of one fenestrule and one dissepiment ; about 24 apertures occur in 10 mm., the distance between the centres of successive apertures being from 0·38 to 0·45 mm. (average 0·41 mm.). The dissepiments broaden slightly where they join the branches, and the fenestrules are oval ; the length of the fenestrules is from 0·94 to 1·2 mm. and their width from 0·3 to 0·51 mm. The dissepiments are relatively broad, 0·23 to 0·47 mm. and the length of one fenestrule and one dissepiment is from 1·31 to 1·55 mm. On the reverse surface both branches and dissepiments are rounded, and the dissepiments are almost as thick as the branches (about 0·5 mm.). The striated layers show about six strong longitudinal striæ ; the outermost layer is covered by small tubercles, but is relatively thin and the striated layers may show through it. Bifurcation occurs at intervals of about 2 cm. ; increase to three rows of cells occurs within four fenestrules before bifurcation.

Remarks : Fenestrellina altacarinata, which has similar measurements, is distinguished by its higher carina, the absence of nodes, and the appearance of the reverse surface.

Fenestrellina canthariformis n.sp.

(Text-figure 2A.)

Holotype : 1423, Sydney University Collection, from the Fenestella Shales, Por. 15, Parish of Belford.

Fenestrellina, with two apertures to a fenestrule ; slight carina with very high nodes.

The colony is infundibuliform with the celluliferous surface internal ; the largest specimen shows a diameter of about 8 cm., and the upper surface of the colony is very much folded ; rootlets occur near the base. There are 16 to 17 fenestrules in 10 mm. vertically and 20 to 24 branches in 10 mm. horizontally. On the celluliferous surface the branches slope gradually inwards from the fenestrules, and the carina is formed mainly by the junction of these two sloping surfaces. Very high nodes, $0 \cdot 24$ mm. ($0 \cdot 21$ to $0 \cdot 25$ mm.) apart, occur on the carina. The zoœcial apertures are circular, with a diameter of about $0 \cdot 08$ mm., and are surrounded by a slight peristome. There are two apertures, separated by rather more than twice their own diameter, to each fenestrule, the centres of the apertures being about $0 \cdot 29$ mm. apart ; they do not project into the fenestrules. The fenestrules are rectangular, $0 \cdot 47$ mm. ($0 \cdot 38$ to $0 \cdot 58$ mm.) long and $0 \cdot 21$ mm. ($0 \cdot 16$ to $0 \cdot 25$ mm.) wide. The branches are $0 \cdot 23$ mm. ($0 \cdot 18$ to $0 \cdot 29$ mm.) wide ; the dissepiments expand only slightly where they join the branches, and are $0 \cdot 13$ mm. ($0 \cdot 08$ mm. to $0 \cdot 19$ mm.) wide. On the reverse surface the dissepiments are slightly less thick than the branches ; both are evenly convex. Near the base of the colony the granular layer of the reverse surface is very much increased, so that the total thickness of the branch is about $0 \cdot 5$ mm. instead of about $0 \cdot 3$ mm. The branches bifurcate at relatively infrequent intervals—about 1 cm. ; increase to three rows of zoœcia occurs immediately before bifurcation.

Remarks : From *Fenestrellina fossula* (Lonsdale) and related species this species is separated by its much smaller size. From *F. mimica* (Ulrich) (Pennsylvanian) it is distinguished by its longer fenestrules, and more widely spaced zoœcia and spines. *F. gratiosa* (Moore) (Penn-

sylvanian) shows fenestrules and dissepiments of the same length and shows the same distance between the zoœcia, but is differentiated by the absence of any carina or nodes and by the projection of its zoœcia into the fenestrules. *F. parviuscula* (Bassler) (Permian) shows slightly shorter fenestrules and narrower branches. From *F. horologia* (Bretnall) (Callytharra to Byro Stages, W.A.) it is distinguished by the very different appearance of the celluliferous surface.

Genus Polypora McCoy.

Polypora dichotoma n.sp.

(Pl. XX, fig. 4.)

Holotype : 1419, Sydney University Collection, from the Ulladulla Mudstones, Warden Head, Ulladulla.

Zoœcia in four rows ; four to five zoœcia in the length of one fenestrule and one dissepiment ; small nodes irregularly developed.

The form of the colony is not shown, but was probably infundibuliform ; there are 7 to 8 branches horizontally and rather more than 5 fenestrules vertically in 10 mm. The branches are flattened on the celluliferous surface, and are normally from 0·9 to 1·2 mm. wide, increasing to about 1·6 mm. before bifurcation. The apertures, which are placed on the flat surface of the branches and do not project into the fenestrules, are normally in four rows, with three after, and five before bifurcation. The peristomes are distinct, but are not exserted ; the apertures are subcircular, from 0·16 to 0·22 mm. in diameter, and are separated by more than their own diameter—about 0·4 to 0·5 mm. between the centres of successive apertures. There are three apertures in the length of one fenestrule, with an extra one or two for the dissepiment ; about twenty-three apertures occur in 10 mm. The whole of the celluliferous surface is finely tuberculate. The apertures are frequently closed by a calcareous plate with a central or sub-marginal perforation ; these calcareous plates also show a tuberculate outer layer. Small nodes are irregularly developed. The fenestrules are small and oval, from 0·85 to 1·1 mm. long, and 0·37 to 0·43 mm. wide ; the dissepiments are 0·6 to 0·94 mm. wide, and are not celluliferous. The inner layers of the dissepiments show strong transverse striæ. The branches and dissepiments are of about the same thickness—about·

0·5 mm.—and both are flat to slightly rounded on the reverse surface. The outermost layer of the reverse surface is finely granular. Bifurcation occurs at intervals of about 1 cm.

Polypora triseriata n.sp.

(Pl. XX, fig. 2.)

Holotype : 1420, Sydney University Collection, from the Ulladulla Mudstones, Warden Head, Ulladulla.

Zoœcia in three rows ; four zoœcia in the length of one fenestrule and one dissepiment ; rows of apertures separated by slight ridges, with small nodes.

The form of the colony is not shown. There are 10 branches horizontally, and 5 fenestrules vertically in 10 mm. The branches are about 0·8 mm. in width, and show three rows of zoœcia ; the lateral rows of apertures do not project into the fenestrules. The rows of apertures are separated by slight ridges ; small nodes occur on these ridges, but are not well preserved ; they appear to be more widely spaced than zoœcial apertures. The apertures are circular, 0·16 mm. in diameter, and are separated by about twice their own diameter, the distance between the centres of successive apertures being 0·45 to 0·56 mm. (average 0·49 mm.) In the middle row there are three apertures in the length of each fenestrule, with an extra one opposite each dissepiment, and twenty apertures occur in 10 mm. The fenestrules are elongated and oval, 1·44 mm. to 1·66 mm. in length, and 0·35 to 0·42 mm. in width. The dissepiments, which expand slightly at their junction with the branches, are 0·38 to 0·48 mm. in width, and are slightly convex on the celluliferous surface ; the length of one fenestrule and one dissepiment is 1·9 to 2·1 mm. The reverse surface is not shown. The outer layer of the celluliferous surface is finely tuberculate. Bifurcation occurs at intervals of about 2 cm. ; increase to four, then five, rows of zoœcia occurs about one fenestrule before bifurcation. After bifurcation there are two or three rows of zoœcia.

Remarks : This species is distinguished from *Polypora virga* Laseron by its smaller size, and from *Polypora pertinax* Laseron, *P. woodsi* (Etheridge) and *P. elliptica* Rogers by its larger size and the spacing of the zoœcia.

Polypora multinodata n.sp.
(Pl. XXI, fig. 7.)

Holotype: 1416, Sydney University Collection, from the Fenestella Shales, Por. 15, Parish of Belford.

Zoœcia in four rows; four zoœcia in the length of one fenestrule and one dissepiment; nodes strongly developed.

The form of the colony is not shown; there are 7 to 9 branches horizontally and 4 to 4·5 fenestrules vertically in 10 mm. Large nodes are irregularly developed. The obverse surface of the branch is fairly flat and the zoœcial apertures do not project into the fenestrules. There are normally four rows of apertures, with six before and three after bifurcation, and there are four apertures in the length of one fenestrule and one dissepiment. The apertures are sub-circular, about 0·2 mm. wide, and 0·28 mm. long; small rounded cells, about 0·1 mm. in diameter, are infrequently developed at the surface. The apertures are separated by about their own diameter, the distance between the centres of successive apertures being 0·4 to 0·62 mm. (average 0·52 mm.), and about 19 apertures occur in 10 mm. The fenestrules are sub-rectangular, and are from 1·31 to 2·52 mm. (average 1·96 mm.) long and 0·23 to 0·82 mm. (0·50 mm.) wide. The dissepiments are 0·34 to 0·9 mm. long, and the branches 0·7 to 1·1 mm. wide. The dissepiments are evenly rounded on both surfaces and are about as thick as the branches. The reverse surface is very finely granular, but the inner layers show about fourteen fine longitudinal striæ.

Polypora magnafenestrata n.sp.
(Pl. XX, fig. 5; Pl. XXI, fig. 5.)

Holotype: 1418, Sydney University Collection, from the lower part of the Fenestella Shales, railway cutting, one mile west of Branxton.

Zoœcia in four to five rows; five to eleven zoœcia in the length of one fenestrule and one dissepiment.

The form of the colony is not shown. There are 5 to 7 branches horizontally and 1·5 to 3 fenestrules vertically in 10 mm. The branches are less than 0·5 mm. thick, and are flattened on both the obverse and reverse surfaces. The dissepiments are rounded and are generally not quite as thick as the branches. The zoœcial apertures do not project into the fenestrules; where the surface is worn impressed lines are shown around the apertures. There

are 6 to 8 rows of apertures before and 3 to 4 after bifurcation, the normal number being 4 to 5. The apertures are slightly elliptical—0·18 by 0·23 mm.—and are separated by about twice their own diameter, the distance between the centres of successive apertures being about 0·56 mm. (0·51 to 0·67 mm.); five to eleven apertures occur in the length of each fenestrule. They may be closed by a thick, centrally perforated calcareous plate, and show a slight peristome. Anterior or slightly lateral to the apertures small rounded surface cells about 0·15 mm. in diameter may occur, and when broken away these leave a distinct hollow scar. Nodes very rarely occur. The fenestrules are very long and irregular in length—1·0 to 7·5 mm.—and 0·41 to 1·3 mm. in width. The dissepiments are from 0·32 to 0·56 mm. in width, and the branches 0·8 to 1·4 mm., increasing to 2 mm. before bifurcation. The zoœcia are rhomboidal, about 0·16 to 0·22 mm. in width, and 0·56 mm. long; on the reverse surface the granular layer is very thin; beneath this about ten longitudinal striæ are shown. Bifurcation occurs at intervals of 0·5 to 1·5 cm.; after bifurcation two adjacent branches may coalesce.

Remarks : This species bears a general resemblance to *Polypora gigantea* Waagen and Pichl, but is distinguished by the number of rows of zoœcia and the width of the dissepiments. *P. gracilis* Prout shows four to five rows of cells, but has longer, very irregular fenestrules.

Polypora linea n.sp.

(Pl. XXI, fig. 1.)

[cf.] *Polypora smithi* Etheridge, 1892, Geology and Palæontology of Queensland and New Guinea, p. 219, Pl. 9, fig. 1, not figs. 2, 3, not Pl. 44, figs. 9, 10.

Holotype : 1414, Sydney University Collection, from the Fenestella Shales, Por. 126, Parish of Mulbring.

Zoœcia in five rows ; six to nine zoœcia in the length of one fenestrule and one dissepiment ; large nodes infrequently developed.

The form of the colony is not known; there are 6 to 7 branches horizontally, and 2·5 to 3 fenestrules vertically in 10 mm. The branches are slightly rounded on the celluliferous surface, but the lateral rows of apertures do not project into the fenestrules; there are normally five rows of apertures, with seven to eight just before, and four

just after bifurcation. The apertures are circular, about 0·22 mm. in diameter, and the peristomes are fairly well marked ; they are separated by about one and a half times their own diameter, the distance between the centres of successive apertures being 0·43 to 0·6 mm. ; there are about twenty apertures in 10 mm. : six to nine apertures occur in the length on one fenestrule and one dissepiment. Large nodes are developed irregularly, usually in about the middle line of the branch. The branches are about 1·2 mm. in width ; the fenestrules are narrower than the branches—from 0·56 to 1·04 mm. wide—and are from 2·9 to 3·8 mm. in length. The dissepiments are from 0·27 to 0·32 mm. wide, and are not celluliferous. On the reverse surface the branches are flattened and the dissepiments rounded ; the branches, which are slightly thicker than the dissepiments, are about 0·4 mm. thick. The cells are long and narrow, about 0·55 mm. long and 0·18 mm. wide. Small, rounded surface cells occur irregularly ; they are placed generally lateral to a zooecial aperture and are about 0·15 mm. in diameter. Bifurcation occurs at intervals of about 2 cm.

Remarks : From *Polypora magnafenestrata* this species is distinguished by its smaller, regular fenestrules, and by its much more abundant nodes. *P. megastoma* de Koninck from the Middle Productus Limestone, shows fenestrules of similar length but the branches and fenestrules are broader, and the number of rows of zooecia greater in the Salt Range form. One of the figures of *Polypora smithi* given by Etheridge (1892, p. 219, Pl. 9, fig. 1, not Pl. 9, fig. 2, 3, not Pl. 44, figs. 9-10) resembles this species : the description and figures, however, cover more than one form. From *P. vancouverensis* Fritz this species differs in its larger fenestrules, and in having five, instead of six, rows of zooecia, and more zooecia to a fenestrule ; *P. brouweri* Bassler, from the Permian of Timor, is a larger form.

<div align="center">

Family ACANTHOCLADIIDÆ Zittel.

Genus Ptilopora McCoy.

Ptilopora carinata n.sp.

(Pl. XXI, fig. 2, text-figure 3.)

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Holotype : F.300, Australian Museum Collection, from the Upper Marine Series, Shoalhaven Heads.

Zooecia in two rows ; slight carina with small nodes : midrib only slightly broader than the branches ; six to seven

branches given off on either side of the midrib in 10 *mm.*;
dissepiments thin, distant.

The specimen shows several fronds apparently belonging
to the one colony ; the midribs are up to 8 cm. in length,
and from 0·56 to 0·67 mm. in width ; they bifurcate
infrequently ; near the apex of each frond the midrib is
thinner but the width is uniform over the greater part of
the length. The lateral branches, which are generally
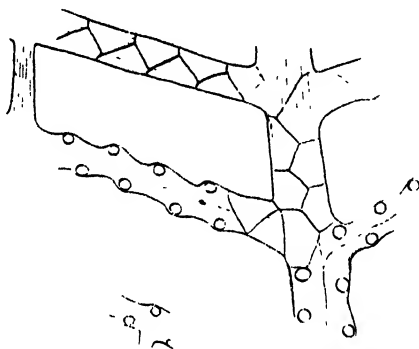
Text-figure 3. *Ptilopora carinata.*

Celluliferous surface of portion of the zoarium. (*Camera lucida*
diagram.)   ×10.

alternating but may be given off at the same level on
opposite sides of the midrib, are from 0·37 to 0·45 mm.
in width near their origin and taper gradually ; the length
of the branches does not generally exceed 1 cm. ; the
distance between the points of origin of successive branches
is from 1 to 2 mm. ; six to seven branches are given off
in 10 mm., the angle between each branch and the midrib
being about 70°. The branches are connected at intervals
of from 1·5 to 3·0 mm. by thin, non-celluliferous dis-
sepiments, from 0·11 to 0·16 mm. in width, and placed at
right angles to the branches. On the celluliferous surface
both midrib and branches show two rows of zoœcial
apertures, separated by a median, not very high and rather
wavy carina, formed chiefly by the junction of the two
sloping sides of the branches. Nodes are developed, but
are not well preserved ; they are not very high, and are
separated by a distance about equal to that between the
zoœcial apertures. The zoœcial apertures are circular,
about 0·14 mm. in diameter ; they are surrounded by

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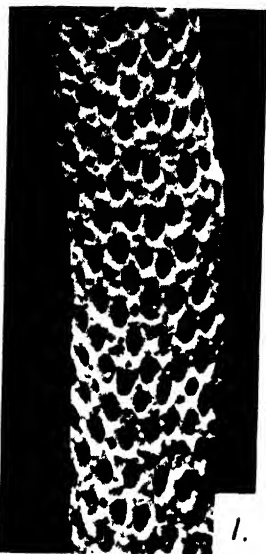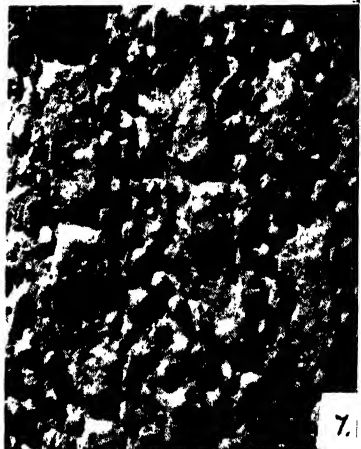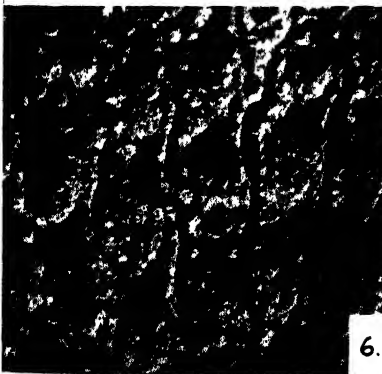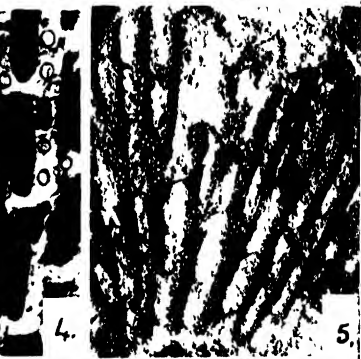
a slight peristome and are raised well above the surface of the branches; where the specimens are weathered this gives the edges of the branches a serrated appearance. The apertures are alternating and separated by the same distance—0·46 to 0·56 mm. between the centres of successive apertures—on both branches and midrib. The cells are triangular to rhomboidal in outline on the basal plate. The innermost layer of the reverse surface showed about six longitudinal striæ; the outer layers are not shown. The dissepiments are rounded, and show fine striæ parallel to their length.

<div align="center">

Family RHABDOMESONTIDÆ Vine.

Genus Rhombopora Meek.

Rhombopora filiformis n.sp.

(Pl. XX, fig. 3.)

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Holotype: 1425, Sydney University Collection, from the Ulladulla Mudstones, Warden Head, Ulladulla.

Zoœcia in ten longitudinal and in well-marked diagonal rows; apertures elongate, five in 3 mm.; acanthopores in a single row on the interspace between adjacent zoœcia.

The zoarium is ramose, branches of the same diameter as the main stem (0·75 to 0·9 mm.) being given off at right angles; the branches are circular in cross section. The zoœcial apertures are arranged in ten longitudinal rows, and in diagonal rows. There are five zoœcial apertures in one longitudinal row in 3 mm. The apertures are elongate-oval, 0·35 to 0·4 mm. in length and 0·08 to 0·13 mm. in width, and are separated by about their own length. The apertures slope inwards steeply proximally but gently distally; the walls are thickened for about one-third of the radius and the bending of the tubes between the mature and immature regions is not very sharp. Diaphragms and hemisepta are not shown. Acanthopores are well developed and are arranged in single longitudinal lines between the apertures, about nine occurring in each line between the proximal ends of two successive apertures. One (sometimes two) additional acanthopores are placed between these rows at the end of each aperture.

Remarks: The narrow zoarium, large, widely-spaced apertures, and number of rows of apertures of this form distinguish it from most other species. *Rhombopora muralis* Moore (1929, p. 141), which it resembles in the

diameter of the zoarium and in the number of rows of apertures, shows much more closely spaced rounded apertures and a different arrangement of the acanthopores.

ACKNOWLEDGMENTS.

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DESCRIPTION OF PLATES.

PLATE XX.

Fig. 1.—*Batostomella cylindrica*. Surface of a slightly weathered topotype (1428, Sydney University Collection). ×10.

Fig. 2.—*Polypora triseriata*. Celluliferous surface of the holotype. ×10.

Fig. 3.—*Rhombopora filiformis*. Holotype. ×10.

Fig. 4.—*Polypora dichotoma*. Celluliferous surface of the holotype. ×10.

Fig. 5.—*Polypora magnafenestrata*. Celluliferous surface of the holotype. ×10.

PLATE XXI.

Fig. 1.—*Polypora linea.* Cast of the celluliferous surface (holotype).
   ×10.

Fig. 2.—*Ptilopora carinata.* Portion of the holotype. Natural size.

Fig. 3.—*Fenestrellina quinquecella.* Celluliferous surface of the holotype.   ×10.

Fig. 4.—*Fenestrellina granulifera.* Celluliferous surface of the holotype.   ×10.

Fig. 5.—*Polypora magnafenestrata.* Celluliferous surface of a specimen from Mulbring (1417, Sydney University Collection).   ×2.

Fig. 6.—*Fenestrellina altacarinata.* Cast of the celluliferous surface (holotype).   ×10.

Fig. 7.—*Polypora multinodata.* Cast of the celluliferous surface (holotype).   ×10.

1-HYDROXYACRIDINE AS A CHELATE COMPOUND.

By Douglas Haig Freeman, B.Sc.,
and Francis Lions, B.Sc., Ph.D.

Bidentate chelate compounds which coordinate through one primary valency and one secondary valency very frequently form non-ionized metallic complexes—the so-called " internal complex salts "—many of which are distinguished by their insolubility in hydroxylic solvents. Such chelate compounds can, consequently, often be utilised in analytical chemistry for quantitative precipitation and estimation of certain metallic ions. Perhaps no such substance has proved of greater importance in recent years than 8-hydroxyquinoline (I)—" Oxine ".
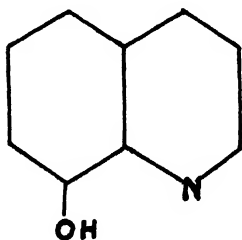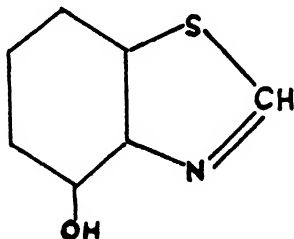
I   II

Numerous researches have thoroughly established its value in analytical chemistry (cf. e.g. Berg, *Z. Anal. Chem.*, 1927, *70*, 341 ; *71*, 23, 171, 321, 361 ; *72*, 177 ; 1929, *76*, 191 ; Hahn and Vieweg, *ibid.*, 1927, *70*, 122 ; Hahn and Hartleb, *ibid.*, *71*, 225 ; Kolthoff and Sandell, *J.A.C.S.*, 1928, *50*, 1900 ; Niessner, *Z. Anal. Chem.*, 1929, *76*, 135 ; Berg and Teitelbaum, *ibid.*, 1930, *81*, 1 ; Geilmann and Weibke, *Z. Anorg. Chem.*, 1931, *199*, 120, 347 ; Halberstadt, *Z. Anal. Chem.*, 1933, *92*, 86 ; Fleck and Ward, *Analyst*, 1934, *59*, 325).

The great usefulness of 8-hydroxyquinoline suggests that the juxtaposition of the phenolic hydroxyl group and the basic tertiary nitrogen atom of the attached fused heterocyclic ring, makes available a specially valuable chelate grouping and suggests the trial of similarly constituted substances.   This idea has already been exploited by Erlenmeyer and Ueberwasser (*Helv. Chim. Acta*, 1938, *21*, 1695 ; cf. also *Helv. Chim. Acta*, 1938, *21*, 709), who prepared several metallic derivatives of 4-hydroxybenzthiazole (II), and showed that this substance was quite suitable for the quantitative estimation of zinc, copper and nickel.

The present paper records the results of some preliminary experiments with 1-hydroxyacridine (III) (" 1-Acridol "), which may be regarded as a " Benzoxine ", and might well be expected to give co-ordination complexes similar
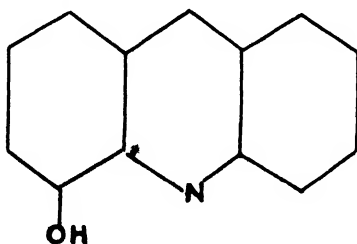
III

in type to those yielded by 8-hydroxyquinoline.   An exhaustive study of 1-acridol (II) as a reagent in qualitative and quantitative analysis has not been carried out, but sufficient results have been accumulated to show that it does behave similarly to " Oxine " (II), forming numerous water-insoluble metallic complex derivatives, whilst, at the same time, differing from II in its behaviour to certain metallic ions, notably that of aluminium.   It seems, therefore, that 1-acridol may prove to be a supplementary reagent in analysis of some value, and since one of the authors is unable to continue the work it is deemed advisable to place the results so far obtained on record.

Treatment of dilute aqueous solutions, containing also sodium acetate and acetic acid, of salts of the metals listed below with 2% alcoholic 1-acridol solution led to precipitation of insoluble metallic complexes : copper, zinc, lead, nickel, ferrous iron, ferric iron, chromium, cobalt, cadmium,

manganese, mercury and thallium. Careful analysis showed that the complexes derived from copper, lead, zinc, nickel and ferrous salts are of the type IV, the metal being
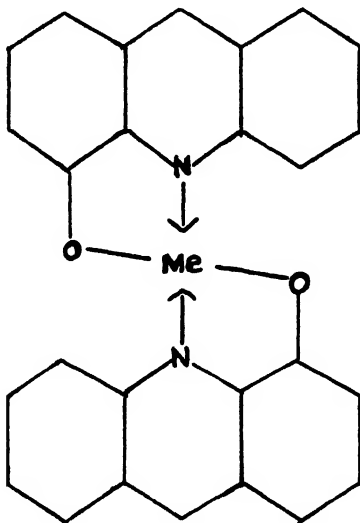
IV

quadricovalent. The complex derived from ferric salts was apparently identical with that derived from ferrous salts, reduction by some of the 1-acridol of the ferric ion to the ferrous state apparently preceding co-ordination. Oxiation of 1-acridol also appeared to occur with silver salts, the dark brown insoluble silver complex precipitated from weakly acid acetate solution being found to contain free silver, and to be of indefinite composition.

The analytical figures obtained for the complexes precipitated from cobaltous, cadmium and manganous salt solutions, indicated that these also were probably of type IV, but in each instance the values found for carbon and nitrogen were considerably lower than theoretical. It is also possible that the salts of type IV were contaminated with basic salts, but insufficient results are available for any definite conclusion concerning the low analytical figures. The chromium complex appeared to be of the type V, similar to the chromium complexes described by Drew and Fairbairn (*J.C.S.*, 1939, 823-35).

$H_2O \longrightarrow Cr \longleftarrow H_2O$

OO C. CH_3

V
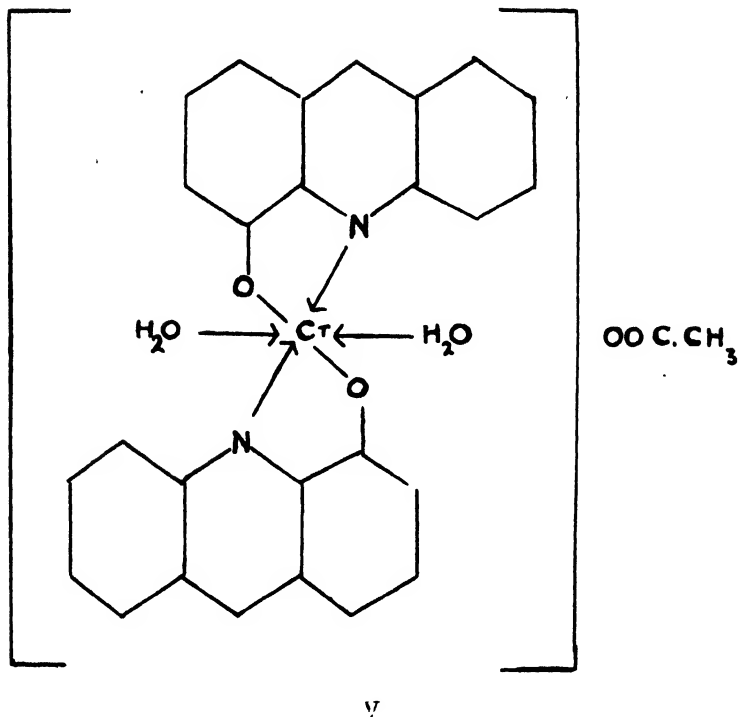
EXPERIMENTAL.

1-Acridol. Two methods for the preparation of 1-acridol appear to have been recently described—by Matsumura (*J.A.C.S.*, 1927, *49*, 816) and by Jensen (*J.A.C.S.*, 1928, *50*, 1144). Eventually 1-acridol was prepared by a modification of Matsumura's method. The starting material, o-anisidine, was converted to 1-methoxyacridine, and by heating this with large quantities of hydriodic acid 1-acridol was obtained in 60% yield. After repeated recrystallisation from 75% aqueous alcohol it formed yellow crystals melting at 116°.

In the preparation of the metallic complexes of 1-acridol a procedure similar to that recorded for the precipitation of metallic complexes with 8-hydroxyquinoline was employed. The method is indicated in the description of the precipitation of the copper complex.

Copper Bis 1-Acridylate (IV. Me=Cu.) Sodium acetate (15 g.) and glacial acetic acid (15 ml.) were added to a solution of crystalline copper sulphate (1·18 g.) in water (300 ml.) at approximately 60°. A 2% alcoholic 1-acridol solution was then stirred in, drop by drop, until it was present in slight excess (up to 10% excess), and the temper-

ature was gradually raised to 90° when the precipitation was apparently complete. The dark red precipitate was collected, thoroughly washed with hot water, then extracted with hot alcohol (to remove any adherent 1-acridol), again washed with hot water and then dried, finally at 140°.

Found: $Cu=13\cdot7$, $C=68\cdot9$, $H=3\cdot7$, $N=6\cdot1\%$; calculated for $C_{26}H_{16}O_2N_2Cu$, $Cu=14\cdot1$, $C=69\cdot1$, $H=3\cdot5$, $N=6\cdot2\%$.

Lead Bis-1-Acridylate (*IV. Me=Pb.*) The lead complex was precipitated quantitatively by adding 2% alcoholic 1-acridol solution (80 ml.) drop by drop with good stirring to a solution of lead nitrate ($0\cdot93$ g.) in water (200 ml.) containing 5% sodium acetate and acetic acid as before. After washing as before with water and alcohol the rust-red granular product was dried at 110°.

Found: $Pb=34\cdot9$, $C=53\cdot2$, $H=2\cdot7$, $N=4\cdot7\%$; calculated for $C_{26}H_{16}O_2N_2Pb$, $Pb=34\cdot8$, $C=52\cdot4$, $H=2\cdot7$, $N=4\cdot7\%$.

Ferrous Bis-1-Acridylate (*IV. Me=Fe.*) Addition of 2% alcoholic 1-acridol solution (50 ml.) to a dilute solution of ferrous ammonium sulphate ($1\cdot41$ g.) containing 5% sodium acetate-acetic acid led to complete precipitation of a black complex which was slightly soluble in alcohol. After boiling with alcohol it was recovered as a dark brown product and was eventually dried at 110°.

Found: $Fe=11\cdot7$, $C=68\cdot9$, $H=3\cdot7$, $N=6\cdot2\%$; calculated for $C_{26}H_{16}O_2N_2Fe$, $Fe=12\cdot6$, $C=70\cdot3$, $H=3\cdot6$, $N=6\cdot3\%$.

The same product was apparently obtained by addition of 2% alcoholic 1-acridol solution to dilute ferric chloride solution ($0\cdot47$ g., $FeCl_3 6H_2O$ in water (200 ml.) containing 5% sodium acetate-acetic acid) or to a similar ferric alum solution. In each instance a black precipitate slightly soluble in alcohol was thrown down.

Found: $Fe=11\cdot8$, $C=68\cdot2$, $H=3\cdot6$, $N=6\cdot1\%$; calculated for $C_{26}H_{16}O_2N_2Fe$, $Fe=12\cdot6$, $C=70\cdot3$, $H=3\cdot6$, $N=6\cdot3\%$.

Nickel Bis-1-Acridylate (*IV. Me=Ni.*) The nickel complex came down, apparently quantitatively, as a deep red precipitate. After washing and drying at 110° it was analysed.

Found: $Ni=11\cdot4$, $C=67\cdot7$, $H=3\cdot8$, $N=6\cdot0\%$; calculated for $C_{26}H_{16}O_2N_2Ni.H_2O$, $Ni=12\cdot6$, $C=67\cdot1$, $H=3\cdot9$, $N=6\cdot0\%$.

It appears, therefore, to contain one molecule of water of crystallisation.

Zinc Bis-1-Acridylate (*IV. Me=Zn.*) This zinc complex was precipitated by the standard method as an orange powder, and did not appear to come down completely. After washing and drying at 110° it was analysed.

Found: $Zn=15\cdot6$, $C=64\cdot3$, $H=3\cdot7$, $N=5\cdot6\%$; calculated for $C_{26}H_{16}O_2N_2Zn.2H_2O$, $Zn=13\cdot3$, $C=63\cdot8$, $H=4\cdot1$, $N=5\cdot7\%$.

It would appear, therefore, that this zinc complex contains two molecules of water of crystallisation, but owing to the incomplete

precipitation it is possible that some proportion of a basic salt has been precipitated and is contaminating the main product.

Cobaltous Bis-1-Acridylate (*IV. Me=Co.*) An orange precipitate was thrown down apparently quantitatively from buffered dilute cobalt acetate solution with alcoholic 2% 1-acridol solution. After washing and drying at 110° it was analysed.

Found : $Co=13\cdot2$, $C=65\cdot3$, $H=3\cdot6$, $N=5\cdot7\%$; calculated for $C_{26}H_{16}O_2N_2Co$, $Co=13\cdot2$, $C=69\cdot8$, $H=3\cdot6$, $N=6\cdot3\%$.

Manganous Bis-1-Acridylate (*IV. Me=Mn.*) The manganous complex of 1-acridol was a mustard coloured compound. After washing and drying at 110° it was analysed.

Found : $Mn=13\cdot2$, $C=64\cdot2$, $H=3\cdot6$, $N=5\cdot8\%$; calculated for $C_{26}H_{16}O_2N_2Mn$, $Mn=12\cdot4$, $C=70\cdot4$, $H=3\cdot6$, $N=6\cdot3\%$.

Cadmium Bis-1-Acridylate (*IV. Me=Cd.*) The cadmium complex was precipitated apparently quantitatively from buffered cadmium acetate solution as a bright orange powder. After washing and drying at 110° it was analysed.

Found : $Cd=21\cdot7$, $C=54\cdot4$, $H=3\cdot0$, $N=4\cdot6\%$; calculated for $C_{26}H_{16}O_2N_2Cd$, $Cd=22\cdot3$, $C=62\cdot4$, $H=3\cdot2$, $N=5\cdot6\%$.

Chromium Complex with 1-Acridol (*V*). 2% alcoholic 1-acridol solution (50 ml.) was gradually added to a well stirred solution of chromic sulphate (0·86 g.), sodium acetate (10 g.) and glacial acetic acid (10 ml.) in water (200 ml.). A dark red complex salt was precipitated. It was collected, washed thoroughly with water, and then recrystallised from alcohol and finally dried at 110°.

Found : $Cr=11\cdot8$, $C=61\cdot9$, $H=3\cdot9$, $N=5\cdot2\%$; calculated for $C_{28}H_{23}O_6N_2Cr$, $Cr=9\cdot9$, $C=62\cdot8$, $H=4\cdot3$, $N=5\cdot2\%$.

Complexes of 1-Acridol with other Metallic Ions. Silver acetate solution readily formed a dark brown precipitate with alcoholic 2% 1-acridol solution, but the collected washed and dried precipitate contained over 50% of silver, indicating reduction of some of the silver salt and precipitation of free silver.

In order to ascertain whether complex formation resulted with other metal ions, a few drops of 2% alcoholic 1-acridol solution were added to dilute solutions of several metallic salts, and it was observed that whilst precipitates formed in them under alkaline or neutral conditions these precipitates were sometimes soluble in a solution containing also sodium acetate and acetic acid.

(a) Precipitates Insoluble In Dilute Acetic Acid-Sodium Acetate Solution.

1. Hg+ from mercurous nitrate—deep red gelatinous precipitate.
2. Hg++ from mercuric chloride—light orange precipitate.
3: Tl++ from potassium thallium bromide—brown precipitate.

(b) Precipitates from Neutral Solution—Soluble in Dilute Acetic Acid-Sodium Acetate Solution.

1. $Ca++$ from calcium chloride—yellow precipitate.
2. Uo_2++ from uranylacetate—deep red precipitate.

(c) Precipitates from Alkaline Solution—Soluble in Dilute Acetic Acid-Sodium Acetate Solution.

1. $Ba++$ from baryta—orange precipitate.
2. $Ca++$ from lime water—yellow precipitate.
3. $Mg++$ from magnesium chloride solution containing ammonium chloride and ammonium hydroxide—yellow precipitate.

Some experiments designed to test roughly the sensitivity of 1-acridol as a reagent for the precipitation of certain metallic ions showed that lead in concentrations as low as 10^{-4} grams per ml. and copper in concentrations as low as 10^{-6} grams per ml. gave definite precipitates.

Finally, it should be noted that precipitates could not be obtained from 1-acridol with salts of aluminium, stannous tin, or bismuth, which is quite remarkable because each of them combines freely with 8-hydroxyquinoline.

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THE THERMAL DECOMPOSITION OF ETHYLIDENE BROMIDE.

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Attention was drawn to the pyrolysis of ethylene and ethylidene halides by the theoretical deductions advanced by Sherman and Sun[1] and Sherman, Quimby and Sutherland.[2] The latter predicted that in the case of ethylene dibromide and ethylidene bromide the reaction should proceed according to the following equation :

$$C_2H_4Br_2 \rightarrow C_2H_4 + Br_2$$
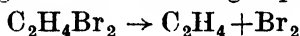
most probably by a halogen-atom catalysed mechanism. The latter authors emphasised that the reaction must be carried out in the gas phase, in the absence of possible catalysts or inhibitors such as oxygen, water vapour, wall effects and light. Although these conditions are difficult to obtain in practice, the conclusions of Sherman were opposed to the results of Sokownin and Zinewsky,[3] who found that in the liquid state between 300° and 400° C. ethylidene bromide, after several hours' heating, reaches an equilibrium with its isomer ethylene dibromide. They assumed the following to be the mechanism of the change :

$$\begin{array}{ccc} CH_3 & CH_2 & CH_2Br \\ | & \rightleftharpoons \| & + HBr \rightleftharpoons | \\ CHBr_2 & CHBr & CH_2Br \end{array}$$
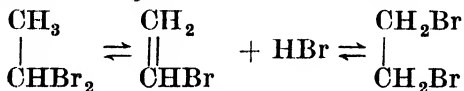
The work of Iredale and Maccoll[4] on ethylene dibromide also indicated that the reaction products would by analogy be vinyl bromide and hydrogen bromide.

With the object of eliminating wall effects, the reaction vessel was used continuously without being cleaned out. By this means it was hoped to reduce the activity of any centres on the glass. Ogg and Polanyi[5] considered a carbon film to be necessary for reproducing the results, whereas Daniels[6] thought a scrupulously clean vessel was essential. However, after further work Daniels states[7] that measurements made with coated walls are

considerably more reproducible. Daniels[7] also showed that, although the rate of decomposition varies with the type of surface, the activation energy is independent of the surface.

With these facts in mind, it was decided to carry out the decomposition of ethylidene bromide in a 250 c.c. pyrex flask, the walls of which had been seasoned by contact with the reaction products at the temperature of the experiments. In this manner an activation energy could be calculated for the reaction.

EXPERIMENTAL METHOD.

Ethylidene bromide was prepared by a modification of the method of Paterno and Pissati[8] and Perkin,[9] namely the action of phosphorus dibromo-trichloride on acetaldehyde. The flask containing the PCl_3Br_2 was cooled while paraldehyde was slowly run in. The red solution became clear as the reaction approached completion. On the addition of water to the mixture, charring set in and a black viscous tar was obtained. Treatment with a small quantity of iced water produced the same result. So the mixture was poured on to a large quantity of chopped ice, the water being removed by a syphon, so that the phosphorus oxychloride and ethylidene bromide were kept in contact with the ice. After 15 to 20 washings with water, followed by sodium carbonate, a milk-white product was obtained and dried over anhydrous sodium sulphate. On fractional distillation the fraction boiling between 105° and 110° C. was collected. This was dried over phosphorus pentoxide, twice fractionated, and a liquid of boiling point 107·3° C. and refractive index n_D^{20} 1·5136 was obtained.

The course of the reaction was studied by following the rate of pressure increase with respect to time. The temperature was kept constant to within 0·5° C. by a manually controlled lead-tin thermostat, and was measured by a platinum resistance thermometer. As the hydrobromic acid would have had a corrosive action on mercury, a glass diaphragm gauge (Fig. 1) had to be employed. A number of these gauges have been described and the one chosen was a modification of that of Karrer, Wulf and Johnson.[10]

The reaction vessel A was joined to a very thin diaphragm B, prepared by blowing a thin bulb and flattening out the end. A glass frame C was joined on to support the platinum wires D. The longer wire just pressed against the diaphragm so as to follow its motion. An outer jacket E was then sealed on and the platinum wires led through the top and sealed. The side arm F permitted the adjustment of the platinum contacts. The isolation of the reacting system was accomplished with tap G, while the side arm H facilitated handling of the
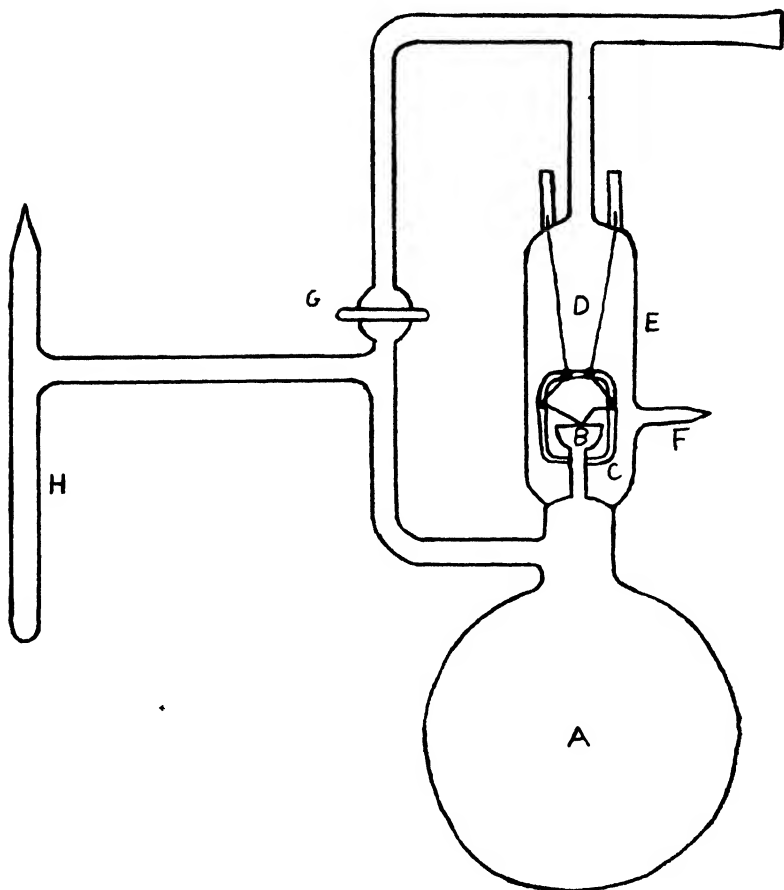
FIG. I.

reacting substances. During a run the side arm was electrically heated to prevent any condensation of the vapour.

The procedure was as follows : With taps G, J, L, O open and liquid air surrounding the trap K, the apparatus was pumped out for three or four hours. The system was then flushed out with nitrogen three times and left at atmospheric pressure. A known volume of ethylidene bromide was introduced into H, cooled with liquid air and sealed off. The system was then evacuated. Tap G was closed and air admitted to the external system until the platinum contacts just broke

a circuit. The manometer reading gave the gauge zero which was subtracted from all future pressure readings to give the true pressure. The ethylidene bromide was evaporated into the vessel and the pressure measured as a function of time. When a steady pressure had been reached indicating the conclusion of the reaction, the products were condensed in H and either distilled over to K or pumped off past P by a combined McLeod gauge-Toepler pump. The system was then exhausted for the next run.

Pyrex.   Glass.
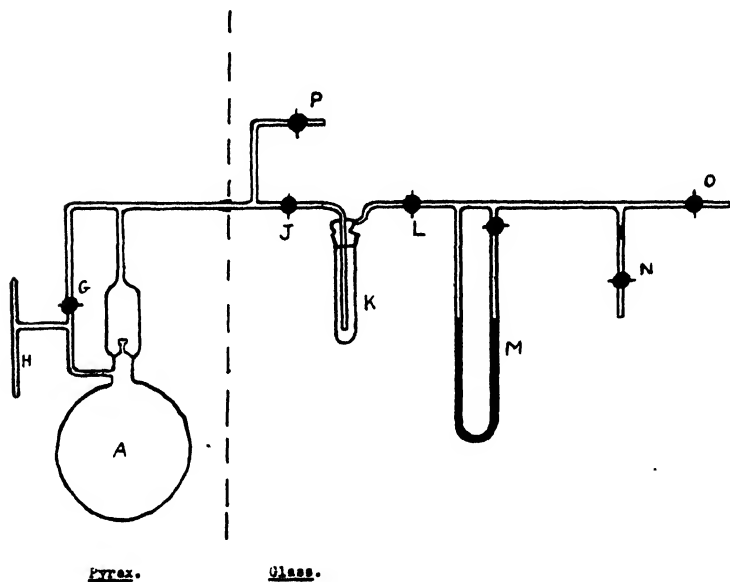
FIG.2.

CALCULATIONS.

The reaction considered

$$C_2H_4Br_2 \rightleftharpoons C_2H_3Br + HBr$$

is seen to have a first order forward reaction and a second order reverse reaction. Kinetically, if [X] represents the concentration of X

$$-\frac{d}{dt}[C_2H_4Br_2] = k[C_2H_4Br_2] - k'[C_2H_3Br] \times [HBr]$$

At equilibrium $-\dfrac{d}{dt}[C_2H_4Br_2] = 0.$

Therefore $K = \dfrac{k}{k^1} = \dfrac{[C_2H_3Br] \times [HBr]}{[C_2H_4Br_2]}$

and $-\dfrac{d}{dt}[C_2H_4Br_2] = k[C_2H_4Br_2] - \dfrac{k}{K}[C_2H_3Br][HBr]$

Now since at constant volume the concentration of each gas is proportional to its partial pressure, this equation can be transformed to pressures.

Let p_1 be the initial pressure of ethylidene bromide,

p_t be its pressure at time t,

p_f the final pressure of the system.

Then $(p_1 - p_t)$ equals the pressure of vinyl bromide, equals the pressure of hydrogen bromide.

If the total pressure at time t is P,

$$P = p_{C_2H_4Br_2} + p_{C_2H_3Br} + p_{HBr}$$
$$= p_t + p_1 - p_t + p_1 - p_t$$
$$= 2p_1 - p_t$$

or $p_t = 2p_1 - P$

So $-\dfrac{dp_t}{dt} = kp_t - \dfrac{k}{K}(p_1 - p_t)^2$

or $-\dfrac{d}{dt}(2p_1 - P) = k(2p_1 - P) - \dfrac{k}{K}(P - p_1)^2.$

If the reaction goes to completion,

$$2p_1 = p_f \text{ and } K = \infty.$$

Now from the results it is seen that $2p_1$ approximately equals p_f, and so the reverse reaction may be neglected. Log $(2p_1 - p_t)$ was plotted against t and the slope of the line multiplied by $2 \cdot 3$ to give the velocity constant.

To determine $2p_1$ and P accurately, the curve P against t was plotted on a large scale and interpolated values of P read from the smooth curve (Fig. 3). The initial pressure was obtained by extrapolation and must be of reasonable accuracy, since the first pressure reading was usually taken about a minute after vaporising.

Regarding the variation of k with temperature, the data was fitted to the curve

$$\ln k = A - \dfrac{E}{RT}$$

or $k = s e^{-\frac{E}{RT}}$

This was done by plotting log k against T^{-1} and measuring the slope and the intercept of the straight line obtained.
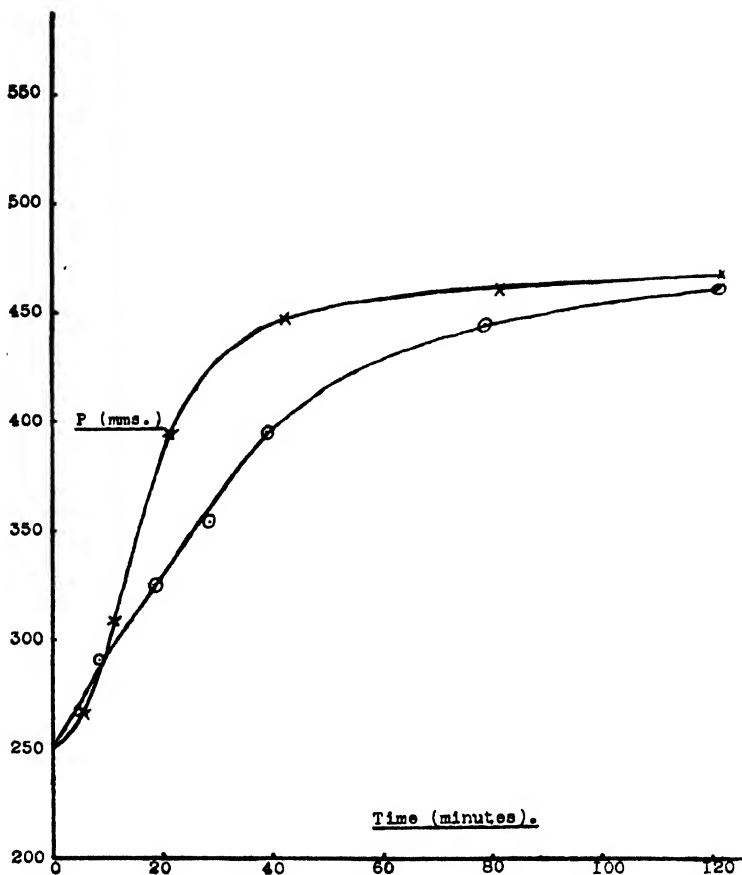
FIG.3

DISCUSSION OF THE RESULTS.

Hydrobromic acid and vinyl bromide were proved to be the products of the reaction, and no trace of bromine could be detected. Although no carbon film was apparent on the surface of the vessel, after a number of runs a black, volatile condensate appeared on the cooler parts of the side arm.

The fact that p_f was usually less than $2p_i$ may be due to either the presence of a reverse reaction or to a reaction involving the products. The effect of variations in p_i

on k is quite marked, but this method appears to be more reliable than that which uses p_f. The assumption made is that the reaction commences so as to proceed to a final pressure $2p_1$, and, if the constants are neglected near the end of a run, no serious error should be introduced by this method. Daniels considers this argument justified. Good straight lines are obtained up to 70% decomposition (Fig. 4), justifying the use of the first order equation.
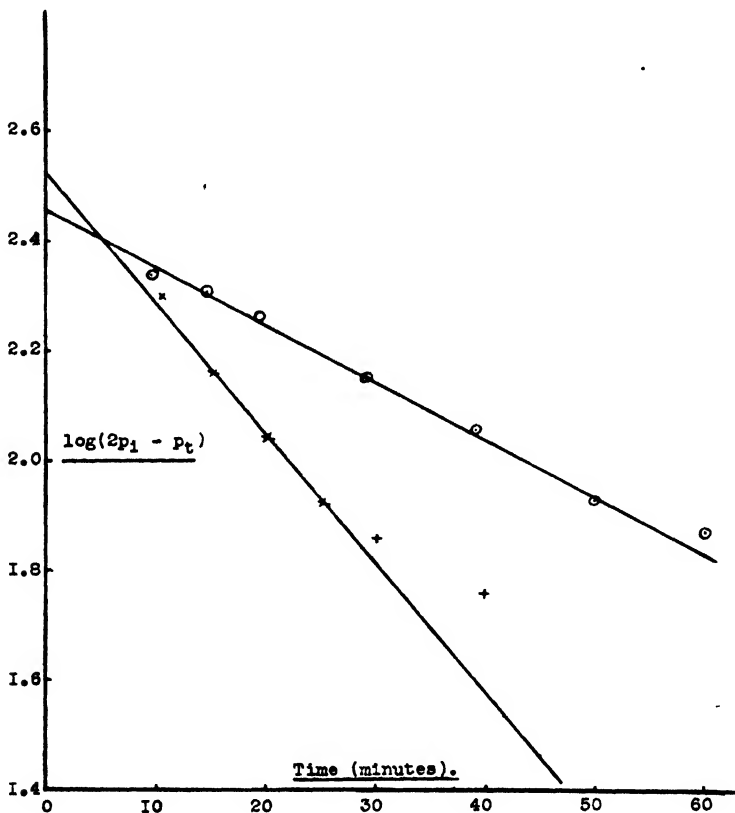
FIG. 4.

The deviations from the mean in a few cases (marked with an asterisk in Table I) may be due to the influence of the decomposition produced during the sealing off of the side arm. It may be significant that in the cases of marked deviation $2p_1$ is very close to or greater than p_f.

TABLE I.—*Pressure-Time Data Interpolated from Large Graphs.*

Experiment	Time (Minutes)												$2p_f$	$k \times 10^4$	Mean
	Temperature 340° C.														
	0	5	10	15	20	25	30	40	50	80	120	160			
2	222	246	252	260	269	280	292	330	362	427	460	476	444	3·93*	3·69
3	250	270	288	306	322	338	356	388	413	447	466	475	500	3·61	
4	245	252	260	272	283	298	312	345	374	428	452	465	490	3·71	
5	259	266	274	282	291	302	316	352	390	447	470	482	518	3·74	
	Temperature 350° C.														
	0	5	10	15	20	25	30	40	50	80	120	160			
13	175	179	186	194	206	222	242	282	301	318	329	338	350	6·14	6·14
15	211	223	236	252	268	290	310	360	381	414	434	443	422	2·88*	
16	231	242	254	270	291	314	342	388	414	445	455	458	462	3·45*	
	Temperature 360° C.														
	0	5	10	15	20	25	30	40	50	80	120	160			
6	260	266	348	382	440	460	472	486	495	508	514	518	520	13·75*	9·18
7	250	268	306	352	392	414	430	442	450	461	468	472	500	9·20	
8	242	254	282	324	368	400	417	431	439	452	458	463	484	9·46	
9	247	258	275	328	370	398	416	431	439	450	458	463	404	9·26	
10	164	214	244	264	278	290	297	303	306	309	311	312	328	8·82	
12	161	168	178	194	218	248	204	282	295	312	321	324	322	5·94*	
	Temperature 380° C.														
	0	2¼	5	7½	10	12½	15	17½	20	25	30	40			
17	258	286	350	422	454	470	477	482	480	494	500	508	516	28·5	28·8
18	238	270	324	387	402	410	416	421	425	431	436	442	478	28·1	
19	234	262	322	376	408	423	430	436	440	446	450	457	468	30·1*	
20	240	280	344	383	408	417	421	425	427	431	438	438	480	23·5*	
	Temperature 400° C.														
	0	½	1	1½	2	3	4	5	6	7	8	10			
21	225	252	280	310	330	355	367	375	380	385	386	390	450	75·7	75·7
22	180	197	207	222	240	280	320	335	345	350	355	363	360	75·7	
23	190	220	240	260	285	335	380	395	—	—	—	—	380	*	

Runs marked * were omitted in taking the mean.

$$\underline{\log\ k\ 10^4}$$

$$\underline{T^{-1}\ 10^3}$$
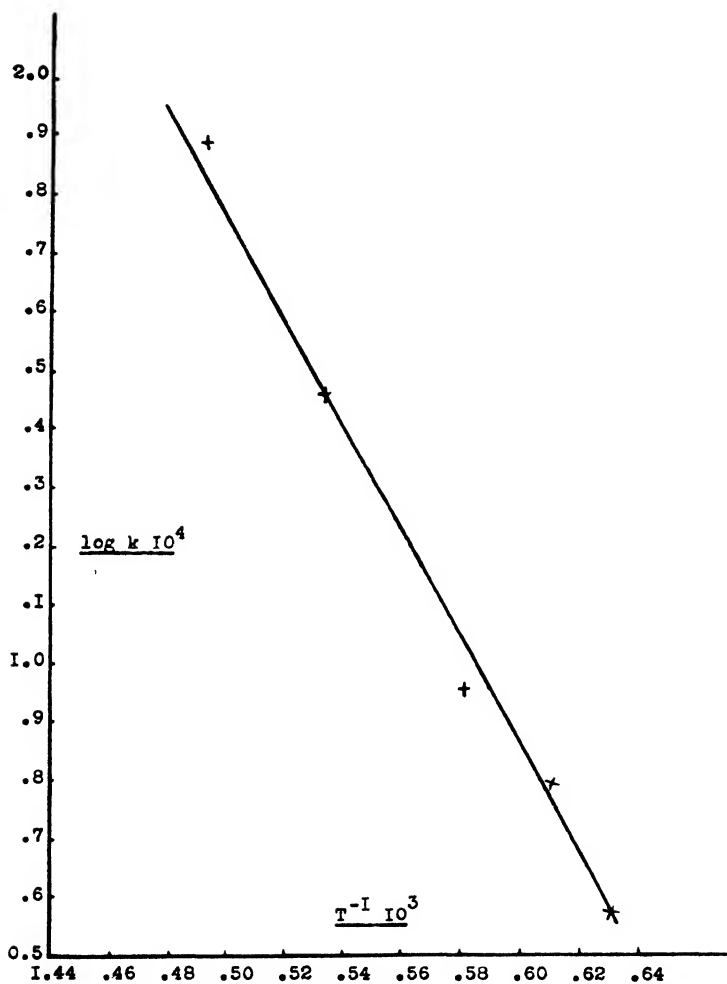
FIG.5

On plotting log k against T^{-1}, the following equations were obtained (Fig. 5):

$$\ln\ k = 25 \cdot 75 - \frac{40900}{RT}$$

$$k = 1 \cdot 57 \times 10^{11} e^{-\frac{40900}{RT}}$$

where the velocity constant is expressed in sec.$^{-1}$.

Regarding the mechanism of the reaction the above data would tend to indicate a pseudo-unimolecular reaction. The fact that there is no pronounced curvature of the $\log k - T^{-1}$ curve shows that there is only one activation mechanism at work, or, what is improbable, two activation processes with the same energy. A possible mechanism is

$$
\begin{array}{cccc}
CH_3 & CH_2\text{-} - \text{-}H & CH_2 & H \\
| & | \quad\quad | & || & | \\
CHBr_2 & CHBr - \text{-}Br & CHBr & Br \\
I & II & III
\end{array}
$$
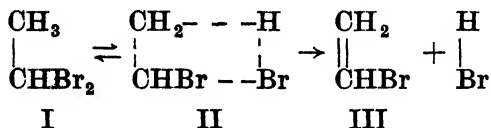
in which the activated complex has the structure II. The resonance energy of the complex would lower the activation energy compared with any such process of the type

$$
\begin{array}{cccc}
CH_3 & CH_3 & CH_2 & H \\
| \rightleftharpoons & | & + Br \rightarrow || & + | \\
CHBr_2 & CHBr & CHBr & Br
\end{array}
$$
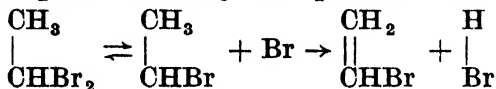
which should have an activation energy comparable with the energy of the C–Br bond (54 Kcals). However, when some bromine was introduced into the reaction vessel in one of the experiments, no marked effect resulted. An alteration in the velocity should have been observed if the latter reaction scheme were correct, as additional bromine atoms would be produced at the temperature of the experiment. The activation energy of $40 \cdot 9$ Kcals is consistent with the first mechanism.

It was found to be impossible to condense out all the resultants after reaction. A rough gas analysis indicated the presence of a small amount of carbon monoxide. It was thought that this might be due to the hydrolysis of a small fraction of the ethylidene bromide by water vapour and the subsequent decomposition of the acetaldehyde. But according to Kassel[11] the decomposition of the acetaldehyde would not proceed with sufficient rapidity at 340-400° C. Also the addition of water vapour did not seem to materially affect the rate.

The presence of a short induction period (Fig. 3) in some of the runs would support the view that the reaction is of the pseudo-unimolecular class. This criticism was made by Semenoff of Daniel's work on ethyl bromide. According to Semenoff[12] this type of reaction is really a chain reaction, the nature of which gives it an approximate first order character.

SUMMARY.

In the range 340-400° C. the thermal dissociation of gaseous ethylidene bromide into vinyl bromide and hydrogen bromide was found to follow an approximate first order law. The velocity constants could be represented by the equation

$$\ln k = 25 \cdot 75 - \frac{40900}{RT}$$

the reaction having an activation energy of $40 \cdot 9$ Kcals.

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ADSORPTION OF HYDROGEN BY AN IDEAL METAL.

By R. C. L. BOSWORTH, D.Sc., F.Inst.P.

Some few years ago J. E. Lennard Jones[1] used the classical picture of a metal as a continuum of electric fluid in order to estimate the heats of (physical) adsorption of certain gases on metal surfaces. The adsorbed atom was regarded as giving rise to an electric image in the metal surface, and the electric interaction between the atom and its image worked out. In this way the attractive fields exerted on the various gases studied were related to their magnetic susceptibilities. In the present paper an attempt will be made to use the same method to calculate the electric polarisation produced in the atom by adsorption. Most of the ordinary gases are known to give electronegative films on clean metals. This means that in the adsorption process the nucleus of the atom is drawn closer to the metal surface than the centre of gravity of the electron charge surrounding it. The present paper will show that the perturbation produced in the normal orbitals of a hydrogen atom by an image field will produce just such a change.

The interaction between the hydrogen atom and the metal surface, replaced by an interaction between the atom and its image, is represented diagrammatically in Figure I. In this figure A represents the nucleus of the hydrogen atom, a distance R from the surface, and B is the electron of coordinates r, θ, φ relative to A. The negative (image) nucleus A' distance $-$R from the surface has a positive satellite electron of coordinates r, $\pi-\theta$, φ relative to A'. The potential energy (v) possessed by the atom due to the presence of its image is, in atomic units,*

$$v = 1/4R + 1/(4R + 4r \cos \theta) - 1/\sqrt{4R^2 + 4Rr \cos \theta + r^2}$$
$$\dots \dots \dots \dots \dots \dots (1)$$

which expression is valid for all $R > 0$.

* One atomic unit of energy is equal to $4\pi^2 me^4/h^2$, $27 \cdot 06$ electron volts; one atomic unit of length $= h^2/4\pi^2 me^2 = 0 \cdot 53 \times 10^{-8}$ cm.
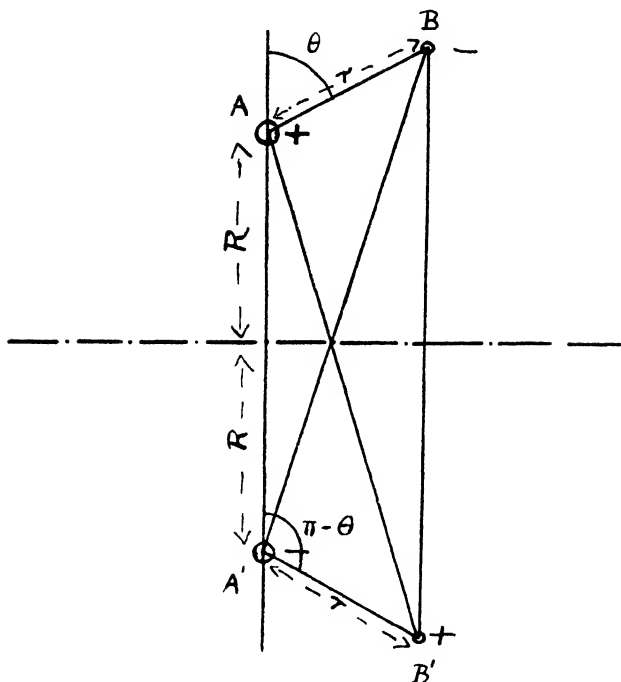
Fig. 1.

We regard now v as a perturbing potential acting on the normal orbitals of the hydrogen atom ; also we regard R as fixed and neglect kinetic energy of the image charges. We assume that we may write the wave function ψ of the perturbed atom as a linear combination of the 1s, 2s and $2p_z$ functions of the normal atom. That is, we put

$$\psi = a_1(\pi)^{-\frac{1}{2}}e^{-r} + a_2(8\pi)^{-\frac{1}{2}}(1-\tfrac{1}{2}r)e^{-\frac{1}{2}r} + a_3(32\pi)^{-\frac{1}{2}}r \cos\theta \, e^{-\frac{1}{2}r}$$

$$\dots\dots\dots\dots\dots (2)$$

where a_1, a_2 and a_3 are undetermined multipliers so to be chosen as to make the energy (E) of the system atom plus image a minimum. Following the usual method it will readily be seen that this is so when

$$\begin{vmatrix} 1+H_{11}-E, & H_{12}, & H_{13} \\ H_{21}, & \tfrac{1}{4}+H_{22}-E, & H_{23} \\ H_{31}, & H_{32} & \tfrac{1}{4}+H_{33}-E \end{vmatrix} = 0$$

$$\dots\dots\dots\dots\dots(3)$$

where H_{11}, H_{12}, etc., are defined by

$$H_{1j}=H_{j1}=\int \varphi_1\varphi_j v r^2 \sin\theta \, dr \, d\theta \, d\varphi \dots\dots\dots(4)$$

and the φ_1's are the three hydrogen wave functions used in defining ψ in equation (2).

The solution of the determinant (equation 3) gives two equations for the a_1's

$$a_1\{H_{23}(E-1-H_{11})+H_{12}H_{13}\}=a_2\{H_{13}(E-\tfrac{1}{4}-H_{22})+H_{12}H_{23}\}$$
$$=a_3\{H_{12}(E-\tfrac{1}{4}-H_{33})+H_{13}H_{23}\}$$
$$\dots\dots\dots\dots\dots(5)$$

a third equation is given by the condition that ψ should be normalised, viz. :

$$a_1{}^2+a_2{}^2+a_3{}^2=1 \dots\dots\dots\dots (6)$$

The dipole moment (μ) of the adsorbed atom is negative if the p_z function reinforces the s function for values of $\theta<\tfrac{1}{2}\pi$, i.e.

$$\mu=-2\int \psi^2 r \cos\theta\, d\tau \text{ atomic units*}$$

$$\mu=-2a_3(256\sqrt{2}/243\, a_1-6a_2) \text{ atomic units}$$
$$=-a_3(8\cdot0\, a_1-32\cdot2\, a_2) \text{ debye units.†}$$
$$\dots\dots\dots\dots\dots (7)$$

The first step in the determination of μ is the evaluation of the matrix hamiltonians H_{1j}. From the definitions $H_{1j}=$

$$\int\frac{\varphi_1\varphi_j}{4R}d\tau+\int\frac{\varphi_1\varphi_j}{4R+4r\cos\theta}d\tau-\int\frac{\varphi_1\varphi_j}{\sqrt{4R^2+4Rr\cos\theta+r^2}}d\tau$$
$$\dots\dots\dots\dots\dots(8),$$

where $d\tau$ of course is written for $r^2 \sin\theta\, dr\, d\theta\, d\varphi$.

The integration is normally to be conducted over all space external to the metal surface. In a preliminary treatment this may be taken as equivalent to all space provided $R>1$ atomic units, as under such conditions little of the electron cloud overlaps the metal surface.

Consider first the H_{11} function. The first integral in equation (8) becomes

$$1/4\pi R\int_0^\infty\int_{0}^{\pi}\int_{-\pi}^{+\pi} r^2e^{-2r}dr \sin\theta\, d\theta\, d\varphi$$

---

* The factor 2 occurs because the electric image gives the same contribution to the dipole moment as the adatom itself.

† 1 Debye unit $=10^{-18}$ E.S.U.'s of dipole moment. 1 atomic unit of dipole moment $=2\cdot67\times10^{-18}$ E.S.U.'s.

which is

$$1/2R \int_0^\infty \int_0^\pi r^2 e^{-2r} dr \sin \theta \, d\theta$$

$$\text{or } 1/R \int_0^\infty r^2 e^{-2r} dr = 1/4R.$$

The third integral is almost equally easy when it is recalled that $1/\sqrt{4R^2 + 4Rr \cos \theta + r^2}$ is the generating function of the Legendre polynomial $P_n(-\cos \theta)$ in $(-\cos \theta)$. A well known property of such polynomials is expressed by the equation

$$\int_0^\pi \cos^m \theta P_n (-\cos \theta) d \cos \theta = 0 \text{ for all } m < n,$$

so that in the calculation of H_{11} it is necessary only to consider $P_0 (-\cos \theta)$ and $P_1 (-\cos \theta)$. The third integral therefore becomes

$$-1/2R \int_0^\infty \int_0^\pi \int_{-\pi}^{\pi+\pi} r^2 e^{-2r} dr \{1 - r/(2R \cos \theta)\} \sin \theta \, d\theta \, d\varphi$$

$$\text{or } -2/R \int_0^\infty r^2 e^{-2r} dr = -1/2R.$$

The second integral, however, is considerably more troublesome. It reads

$$1/4R \int_0^\infty \int_0^\pi \int_{-\pi}^{\pi+\pi} r^2 e^{-2r} dr \, (1/\overline{R + r \cos \theta}) \sin \theta \, d\theta \, d\varphi$$

$$\text{or } 1/2R \int_0^\infty r^2 e^{-2r} dr \int_{-1}^{+1} \left(1 + \frac{r \cos \theta}{R}\right)^{-1} d \cos \theta$$

$$\text{or } 1/2 \int_0^\infty r e^{-2r} \log_e \left| \frac{1 + r/R}{1 - r/R} \right| dr$$

A21

When R is very large the logarithm may be expanded in powers of $1/R$ and this function then reduces to

$$\int_0^\infty (r^2/R + r^4/3R^3 + \ldots)e^{-2r}dr = 1/4R + 1/4R^3 + \ldots$$

so that $H_{11} = 1/4R^3$ for very large values of R.

We are, however, interested in values of R, which, although >1, are not large and accordingly a more accurate solution of the logarithmic integral is required. The integral is first rewritten in the form

$$1/2 \int_0^\infty re^{-2r} \log (1+r/R)dr - 1/2 \int_0^\infty re^{-2r} \log |(1-r/R)| dr$$

which on making suitable substitutions goes over to

$$\tfrac{1}{4}Re^{2R} \int_1^\infty \left(1 + \frac{1/2R - 1}{x}\right)e^{-2R}dx - \tfrac{1}{4}Re^{-2R}\lim_{\varepsilon \to 0}$$

$$\left\{\int_1^\varepsilon \left(1 + \frac{1/2R + 1}{x}\right)e^{2Rx}dx + \int_\varepsilon^\infty \left(1 + \frac{1/2R + 1}{x}\right)e^{-2Rx}dx\right\}$$

or $\tfrac{1}{4}\left[e^{2R}(\tfrac{1}{2} - R)\int_{2R}^\infty e^{-y}/ydy - e^{-2R}(\tfrac{1}{2} + R)\lim_{\varepsilon \to 0}\right.$

$$\left.\left\{\int_{-2R}^\varepsilon e^{-y}/ydy + \int_\varepsilon^\infty e^{-y}/ydy\right\}\right]$$

Now $\int_{2R}^\infty e^{-y}/ydy$ and $\lim_{\varepsilon \to 0}\left\{\int_{-2R}^\varepsilon e^{-y}/ydy + \int_\varepsilon^\infty e^{-y}/ydy\right\}$ are well known integrals and, although they cannot accurately be expressed in any power series, have been tabulated.[2] They are customarily denoted by $-Ei(-2R)$ and $\overline{Ei}(2R)$ respectively. Using this notation the second integral in the H_{11} function reduces to

$$-\tfrac{1}{8}\{e^{2R}Ei(-2R) + e^{-2R}\overline{Ei}(2R)\}$$
$$+ \tfrac{1}{4}R\{e^{2R}Ei(-2R) - e^{-2R}\overline{Ei}(2R)\}$$

The two expressions in curly brackets appear in all calculations of the hamiltonian elements in this problem, so that it is convenient to have a shorthand notation for them. We shall write

$$e^{-a}\overline{Ei}(a) - e^{a}Ei(-a) \text{ as } 2 \text{ Sei}(a) \quad \dots \dots \dots \dots (9)$$

and $e^{-a}\overline{Ei}(a) + e^{a} Ei(-a)$ as $2 \text{ Cei}(a)$ $\dots \dots \dots \dots$ (10)
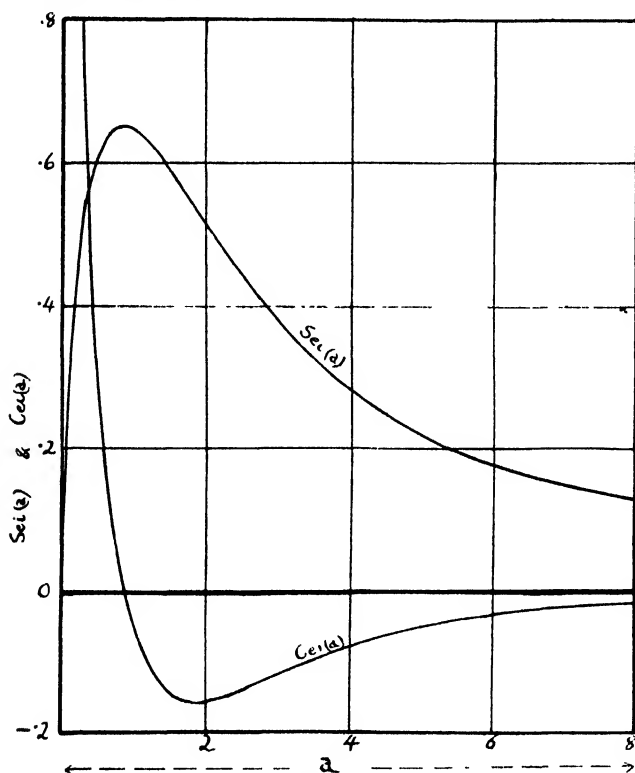
Fig. 2.

Graphs of these two functions have been constructed and are given in Fig. 2. Certain properties of these two functions are obvious from this figure. Thus at $a = 0$ Sei(a) vanishes while Cei(a) is infinite. As a increases Sei(a) at first increases to reach a maximum at $a = 0.86$ and then decreases to zero as a tends to infinity. Cei(a) decreases with increasing a, changes sign at $a = 0.86$, attains a minimum at $a = 1.85$ and thereafter increases to approach the zero value from below as a tends to infinity. Fig. 2

also illustrates properties implicit in the definition of Sei(a) and Cei(a), viz.:

d Sei(a)/da$=$Cei(a) and

d Cei(a)/da$=$Sei(a)$-1/a$ ....(11)

In terms of these two functions H_{11} may be expressed as

$H_{11}=\frac{1}{4}R^{-1}+\frac{1}{4}$ Sei(2R)$-\frac{1}{2}$R Cei(2R) ....(12)

By a similar series of calculations it may be shown that

$H_{22}=-\frac{1}{4}R^{-1}+1/32$ {$(2-R^2)$Sei(R)$+(2R+R^3)$ Cei(R)}
................(13)

$H_{33}=-\frac{1}{4}R^{-1}-3/2R^{-3}-R/16+R^2/32$\{Sei(R)$-$R Cei(R)\}
................(14)

$H_{12}=H_{21}=2^{-\frac{1}{2}}$\{R/9$+(2/27-R^2/6)$ Sei(3R/2)
$+$R/9 Cei(3R/2)\}
................(15)

$H_{13}=H_{31}=2^{-\frac{1}{2}}$\{4/27$+64R^{-2}/243-$R/9 Sei(3R/2)
$-R^2/6$ Cei(3R/2)\}
................(16)

$H_{23}=H_{32}=-1/16-R^2/32-3/4R^2+R^3/32$ Sei(R)
................(17)

At large values of R these elements asymptote to the figures below

$H_{11}=\frac{1}{4}R^{-3}$, $H_{22}=3\cdot5R^{-3}$, $H_{33}=3R^{-3}$, $H_{12}=-0\cdot249R^{-3}$,
$H_{13}=-1\cdot49R^{-4}$ and $H_{23}=22\cdot5R^{-4}$,

all only when R$>$10.

These asymptotic values may be used to calculate the polarisation produced in the hydrogen atom at relatively large distances from the surface. We use the fact that when R is large there is but little perturbation, and $E\simeq1+H_{11}$, so that equations (5) become

$H_{12}H_{13}a_1=0\cdot75H_{13}a_2=0\cdot75H_{12}a_3$,

or $\quad0\cdot37a_1=-1\cdot13$ R$^{-4}a_2=-0\cdot186$ R$^{-3}a_3$
................(19)

i.e. $a_2=-0\cdot33$ R^{-3}, $a_3=-2\cdot0$ R^{-4}, a_1 (of course)$=1$.

Equation (7) then gives for μ the moment of the induced dipole

$\mu=16$ R^{-4} debye units ....(20)

a figure which is of the opposite sign to that recorded by experiments on the adsorption of hydrogen on various metals. Dubois[3] found that the adsorption of hydrogen made certain metals more electronegative. Lukirsky and Ryanoff[4] and also the author[5] recorded that hydrogen increased the frequency of light needed to produce photoelectric emission from a potassium surface (moved the threshold towards the blue end of the spectrum). The

author[6] has also shown that a hydrogen film on tungsten has a negative contact potential relative to the clean surface. However, by the method of approximation used equation (20) is valid only for large values of R, and it may reasonably be expected that in the equilibrium position of the hydrogen atom R is not large. We go back therefore to the more complete expressions for the hamiltonian elements given by equations (12) to (17). Values of each of the six elements have been calculated numerically at selected values of R with the help of the graphs of Sei(R) and Cei(R) given in Fig. 2. From each set of values of the hamiltonians the secular determinant (equation 3) was set up and solved for E. The numerical value obtained was inserted in equation (5) and μ thus found.

As an example we may consider the calculation at R = 2. At this point the H_{ij} have the following values:

$$H_{11} = 0 \cdot 02235 \qquad H_{22} = -0 \cdot 09928 \qquad H_{33} = -0 \cdot 33437$$
$$H_{12} = 0 \cdot 01693 \qquad H_{13} = 0 \cdot 03416 \qquad H_{23} = -0 \cdot 24602$$

The determinant therefore reduces to

$$E^3 - 1 \cdot 08870 \ E^2 - 0 \cdot 00686 \ E + 0 \cdot 07533 = 0.$$

An approximate solution of this equation, by the nature of its derivation, is $1 + H_{11} = 1 \cdot 02235$. By successive approximations the true solutions may be found. They are: $1 \cdot 02350$, $0 \cdot 30584$ and $-0 \cdot 24064$. As the first mentioned solution is the only one corresponding to a bonding energy, it is clearly the one required. Solutions of equations (5) and (6) now follow as

$$a_1 = 0 \cdot 999524, \ a_2 = 0 \cdot 01150, \ a_3 = 0 \cdot 02861.$$

From which

$$\mu = -0 \cdot 218 \text{ debye units.}$$

This figure is of the same sign and of the same order of magnitude as that recorded experimentally.

The results of calculations similar to the one above are shown graphically in Fig. 3, where the interaction energy $(-\phi) = E - 1$, atomic units, and the dipole moment μ are plotted as functions of R. In Fig. 3 the atomic units, so handy in quantum calculations, have been changed to more customary units. R is now expressed in Ångstrom units, E in calories per gram molecule (1 atomic unit of energy per atom = 632,000 calories per gram molecule), and μ, as above, in debye units (1 debye unit = 10^{-18} E.S.U.'s of dipole moment).

Fig. 3 shows that the potential energy of the hydrogen atom comes to a definite minimum at R = $1 \cdot 0$ Å, and this

is the necessary condition that the atom should be bonded to the surface. This minimum represents a bonding energy of 15,200 calories per gram molecule. At this point $\mu = -0\cdot37$ debye units, which therefore is the normal dipole moment associated with a hydrogen atom adsorbed to a metal surface by a pure image field. The fact that the equilibrium R is greater than $0\cdot56$ Å, and also that μ
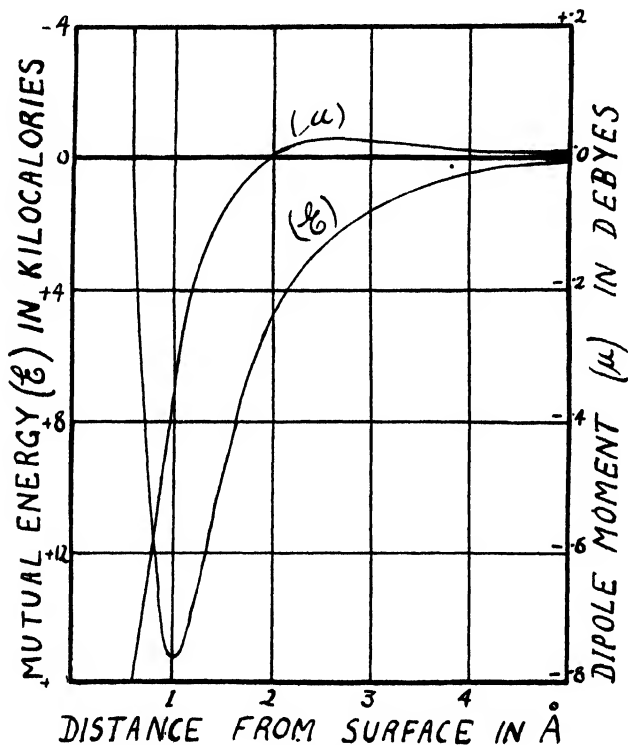
Fig. 3.

is negative, justifies the approximation implicit in the integration of the potential energy terms over all space, as results show that little of the electron cloud overlaps the metal surface.

Before comparing these figures with ones obtained experimentally, it must be noted that the method here employed has made no attempt to associate a periodic structure with the metal surface. We have been concerned with calculating the attraction between a hydrogen atom

and the metal surface as a whole, and not with any particular atom in the surface. Such interaction would presumably cause a still further lowering of the mutual potential energy of the surface and the adsorbed atom. It is therefore to be expected that experimental determinations of the heat of adsorption will be greater than the figure calculated in this paper.

We know as a result of recent studies by a number of authors (Taylor and Langmuir,[8] Bosworth,[9] Fonda, Young and Walker,[10] Johnson and Shockley,[11] Benjamin and Jenkins[12] and others), that atoms adsorbed on a metal surface may exhibit besides the normal static state a mobile state of higher energy content wherein the atom although still bound to the surface is not bound to any particular atom, and is free to wander over the surface. The calculation carried out in this paper may therefore be regarded as an attempt to obtain the heat of adsorption of hydrogen in the mobile state on any metal surface by ignoring the periodic field due to the surface atoms.

There are no experimental figures yet for the heat of adsorption of hydrogen in this mobile state, and indeed only one satisfactory figure for the heat of adsorption of atomic hydrogen on a clean metal—that of 60,000 calories for hydrogen on tungsten obtained by Roberts.[7] We therefore expect that, if the analysis above gives approximately a complete picture of adsorption in the mobile state, an energy increment of $60,000 - 15,200 = 44,800$ calories would be required to raise a static hydrogen adatom to the mobile state. There are indications that this figure is of the correct order of magnitude.

Two figures are available for the experimental dipole moment of hydrogen adsorbed on clean metals. The author[6] obtained $-0 \cdot 42$ debye units for hydrogen adsorbed on tungsten. A photoelectric investigation[5] showed a threshold change of $-0 \cdot 44$ volts produced by the adsorption of hydrogen on potassium. Assuming a one to one packing of the hydrogen atoms on the surface potassium atoms, this means a dipole moment of $-0 \cdot 50$ debye units. These figures are in very satisfactory agreement with the calculated figure of $-0 \cdot 37$ debye units, and indicates on the picture above that the work function of these hydrogen-covered surfaces has but a small temperature coefficient, as any change in dipole moment on activation of an adatom affects its contribution to the work function of the surface. The fact that the

temperature coefficient of the work function of a hydrogen-covered tungsten surface is practically identical with that of a clean surface has already been noted.[6]

A further deduction which may be made from Fig. 3 is that if by any means a hydrogen atom could be held at a distance of 2 Å or more from a metal surface it would be positively polarised by the image field. On bringing up the atom to the surface the electron cloud is initially attracted more strongly than the nucleus. At 2·6 Å this positive polarisation is at a maximum, and on closer approach the dipole moment begins to decrease, becoming zero at 1·8 Å, and on closer approach rapidly becomes more negative.

SUMMARY.

The interaction between a hydrogen atom and its electric image in an ideal metal has been worked out by considering the mutual energy of the atom and its image as a perturbation of the normal hydrogen orbitals. It is found that the interaction energy becomes a minimum when the atom is at a distance of 1·0 Å from the surface, and that the atom adsorbed by this mechanism has a heat of adsorption of 15,200 calories per gram molecule and a dipole moment of −0·37 debye units.

It is suggested that this state of being adsorbed to the surface as a whole and not to any particular atom in the surface may be identified with the mobile adsorbed state. The figures calculated for the properties of this state are not inconsistent with such experimental data as exists.

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ORGANIC ARSENICALS IN PEACE AND WAR.*

By G. J. BURROWS, B.Sc.

Mr. President, Ladies and Gentlemen,

I fully appreciate the high honour that the Society has conferred upon me. I feel, however, that there are some among you who are more worthy of that honour. At the same time, I cannot but feel pleased that it is my privilege to give this lecture tonight, since, as many of you know, it was under the guidance of the late Professor Liversidge that I commenced my studies in chemistry—I was a first year student during his last year at the University. Professor Liversidge was well known to the senior members of the Society on account of the large number of papers he presented for publication in the Society's Proceedings. I can remember him only as the Professor of Chemistry whose lectures I had to attend—lectures full of detail and illustrated with an extraordinary number of experiments. Judging by the extent of his publications, one would conclude that Professor Liversidge must have lived for research. If we, his pupils, have failed to devote as much time to the search for knowledge as we should have done, it is not for want of an example.

I have taken as the title of my address Organic Arsenicals in Peace and War. I do not, however, intend to dissect the subject in the manner that the title might suggest. I propose, in the short time at my disposal, to treat the subject rather from an academic viewpoint and to review briefly some of the methods available for the preparation of organic derivatives of arsenic. At the same time I will use for illustrations compounds which have been of service to man, either as agents of destruction or the reverse.

Today there are many thousands of organic arsenicals known, a fact to be attributed to the ease with which

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carbon-arsenic linkages are formed and also to the stability of such linkages. Once an organic arsenical is prepared, it can be subjected to many diverse types of reaction to yield fresh derivatives without severing the C–As bond. Yet in spite of this ease of formation and stability, the vast number of organic arsenicals are almost exclusively products of the laboratory.

The first organic derivative of arsenic was prepared by Cadet de Gassicourt, who, in 1760, distilled a mixture of arsenious oxide and potassium acetate and obtained a mixture of two oils, the heavier one (cacodyl) being inflammable and possessing a most objectionable odour— so much so that it was not further investigated until 1804. It is interesting to note that during the next fifty years Cadet's fuming oil attracted the attention of such men as Berzelius, Laurent, Dumas, Gerhardt, Bunsen, Frankland and Kolbe. But it was not till 1854 that Cahours and Riche[1] definitely established the constitution of cacodyl and obtained the chloride. Five years later Cahours,[2] by heating methyl iodide with zinc or cadmium arsenite, succeeded in preparing tetramethyl arsonium iodide, and by distilling this with potassium hydroxide he obtained trimethyl arsine. He also prepared tetramethyl arsonium triiodide, and from this, by distillation, he obtained dimethy iodo arsine (cacodyl iodide). And by heating dimethyl iodo arsine with iodine, he finally obtained methyl diiodo arsine, thus completing the series $MeAsI_2$, Me_2AsI, Me_3As and Me_4AsI. Cahours thus laid the foundation of aliphatic arsenical chemistry.

Another example of the high quality of the work of the last century is to be found in the publications of Michaelis. Beginning in 1876 with the preparation of phenyl dichloro arsine by the action of arsenious chloride on mercury diphenyl,[3] he continued his work until 1915, during which period he prepared nearly every type of aromatic arsenical known today, including (in 1881) arsenobenzene,[4] the parent substance of compounds prepared years later by Ehrlich in his quest for successful specifics for the treatment of syphilis, trypanosomiosis and other diseases. The method employed by Michaelis for the formation of an arsenobenzene was essentially the method used today in the preparation of this type of compound, i.e. the reduction of an arsonic acid or an oxyarsine. This type of reaction was subsequently fully exploited by Ehrlich and his co-workers in the preparation of compounds such

as salvarsan and neosalvarsan, the synthesis of which I will refer to later.

I would like to pass on to consider a few of the methods now in use for the preparation of compounds containing carbon-arsenic linkages, and of some of the reactions whereby derivatives of these compounds may be obtained.

ALIPHATIC COMPOUNDS.

(1) Tertiary arsines of the type R_3As are readily prepared by the interaction of Grignard reagents and arsenic halides.[5]   Arsenious iodide has been found to be a most useful reagent for this purpose.   These tertiary arsines on treatment with iodine will yield progressively, compounds of the type R_2AsI and $RAsI_2$.[6]

(2) *Alkylation.*   The alkylation of sodium arsenite was first described by Meyer in 1883, and the method has since been modified by Klinger and Kreutz (1889) and others.[7] When sodium arsenite is treated with methyl iodide in aqueous alcohol, sodium methyl arsonate is formed together with sodium iodide.   Alkylation is due to the tendency of the arsenic atom to pass from the tervalent to 4-covalent state by virtue of the lone pair of electrons present in tervalent arsenic.   On treatment with acid, sodium methyl arsonate yields methyl arsonic acid which is readily reduced in acid solution by hydriodic acid (sulphur dioxide and iodine) to methyl diiodo arsine,[8] from which by treatment with a weak alkali methyl arsenious oxide may be obtained.   This may be dissolved in sodium hydroxide and the sodium methyl arsenite again methylated to yield the sodium salt of dimethyl arsinic acid (cacodylic acid), and from this in turn one can prepare the iodide (or chloride) and oxide.[9]   (See Fig. I.)

Ethylation proceeds quite satisfactorily, but as would be expected is a slower reaction.   The reaction makes possible the preparation of mixed arsines, e.g. sodium arsenite may be methylated and the sodium methyl arsenite obtained after reduction and addition of alkali may then be ethylated giving methyl ethyl arsinic acid from which methyl ethyl iodo arsine[10] may ultimately be obtained.   By coupling these mixed halogeno arsines with suitable Grignard reagents prepared from either alkyl or aryl halides one can readily obtain asymmetrical tertiary arsines in good yield.[11] Iodo arsines react with potassium cyanide[12] yielding cyano arsines and the cyanogen group may be hydrolysed in the ordinary way to carboxyl yielding carboxy arsines.[13]

Arsonic acids may be reduced by means of amalgamated zinc in acid solution to primary arsines, e.g. $MeAsO(OH)_2 \rightarrow MeAsH_2$.[14] Reduction of dimethyl arsenious oxide by platinised zinc in acid solution yields the secondary arsine, Me_2AsH.[15] (Unlike the nitrogen analogues, these arsines do not possess basic properties.)

$$As(ONa)_3 \xrightarrow{MeI} Me\overset{O}{As}(ONa)_2 \longrightarrow MeA\overset{O}{s}(OH)_2$$

$$Me AsI_2 \xleftarrow{\quad HI \quad} \qquad Me AsO \xrightarrow{NaOH} Me As(ONa)_2$$

$$Me AsI_2 \longrightarrow Me AsO$$

$$Me As Cl_2$$

$$Me_2 AsI \longleftarrow Me_2\overset{O}{As} OH \qquad \xleftarrow{MeI}$$

$$\qquad\qquad\qquad\qquad Et\,I \downarrow$$

$$Me_2 As CN \qquad Me Et AsI \qquad \xleftarrow{HI} Me Et AsO \cdot (OH)$$

$$Me_2 As COOH \qquad \xrightarrow{Grignard} R. Me Et As$$
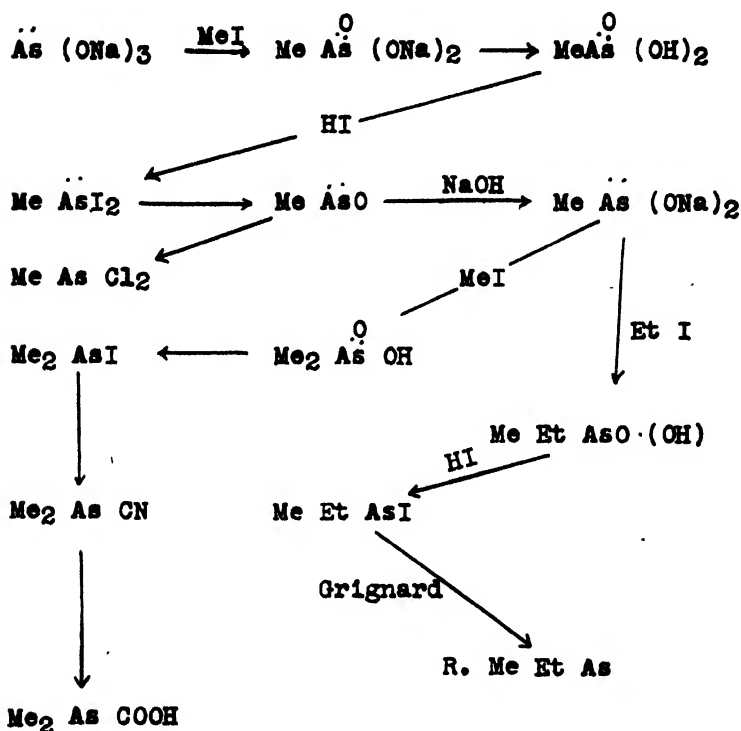
Fig. 1

Ethyl dichlorarsine (b.pt. 156°) was used by the Germans in March, 1918. It is a lung-injuriant agent and also a fairly powerful sternutator and vesicant. A concentration of 0·010 mg. per litre is not tolerable for more than a minute on account of irritation of nose and throat. There is no record of casualties, but on account of its quick action and low persistency it should be suitable for use prior to an infantry offensive. The German method of manufacture was to ethylate sodium arsenite with ethyl

chloride under pressure, followed by reduction by sulphur dioxide in the usual way.

Before leaving the aliphatic compounds I would like to refer to one other special reaction. When acetylene is passed into anhydrous arsenious chloride in the presence of aluminium chloride, a series of compounds is obtained. In 1919 Dafert[16] described a compound, obtained in this way, to which he assigned the formula $AsCl_3.2C_2H_2$. The properties of the substance are similar to those of $\beta\beta'$-dichloro divinyl chloroarsine. Actually the reaction produces a mixture of three compounds :

β chloro vinyl dichloroarsine $ClCH=CHAsCl_2$.

$\beta\beta'$ dichloro divinyl chloroarsine $(ClCH=CH)_2AsCl$.

$\beta\beta'\beta''$ trichloro trivinyl arsine $(ClCH=CH)_3As$.

These compounds were described by Price and Green in 1921[17] but actually they were being manufactured in quantity in America in 1917–18. The most important compound is the first, the dichloroarsine, and in its manufacture the product is fractionated to avoid as far as possible the inclusion of the other two. The product " Lewisite " (b.pt. 190°) has properties very similar to those of mustard gas. It is a strong vesicant and it will pass through ordinary clothing. It is hydrolysed with water yielding hydrochloric acid and chloro vinyl arsine oxide, which also is described as a vesicant. Like mustard gas, it is quickly destroyed by caustic soda, and is easily oxidised. Though much has been claimed for " Lewisite " as a vesicant, it has yet to be tried out under war conditions, as the first shipment from America in 1918 never reached Europe. On account of the armistice, it was dumped at sea.

AROMATIC COMPOUNDS.

(1) As in the case of aliphatic compounds, tertiary arsines are easily prepared by the action of Grignard reagents on arsenious halides.[18] The tertiary arsines may then be degraded by reaction with arsenious chloride to give diaryl mono chloro arsines.[19]

(2) Tertiary arsines may also be prepared by the action of sodium on a mixture of arsenious chloride and aryl halides.[20]

(3) The Bart reaction[21] (1912) probably affords the most important method of preparation of aromatic arsonic and arsinic acids. In this reaction, a diazonium salt is

added to a solution of sodium arsenite in the presence of a suitable catalyst (usually copper sulphate). Nitrogen is evolved on heating, sodium chloride split out and the sodium salt of an arsonic acid obtained. The free arsonic acid is obtained by acidifying the solution of the sodium salt. Many modifications of the original Bart reaction have been described,[22] but experience has shown that if the solution of the diazonium salt is added to the sodium arsenite solution maintained at a temperature of $45°-50°$ C. then the original method generally gives good yields. The arsonic acid may be reduced in hydrochloric acid solution by sulphur dioxide (after the addition of a small quantity of iodine or potassium iodide) yielding a dichloroarsine. On treatment with a weak alkali the dichloroarsine may be converted to the oxy-arsine which will dissolve in sodium hydroxide to give sodium aryl arsenite. This may be coupled with another molecule of a diazonium salt to give a diaryl arsinic acid[23] ($R_2AsO.OH$), which can be reduced as before by sulphur dioxide to give a diaryl mono chloroarsine such as Ph_2AsCl. This sodium aryl arsenite may also be alkylated to give mixed alkyl aryl halogeno arsines[24] of the type $RR'AsX$. (See Fig. 2.) Halogeno arsines will all react with Grignard reagents, and these reactions obviously afford a method of preparation of tertiary arsines[25] in which the arsenic atom may be combined with three different groups. In 1929 Blicke and Smith[26] showed that mixed arsine oxides could be prepared by the action of Grignard reagents on aryl arsine oxides dissolved in benzene. Thus from p-tolyl magnesium bromide and phenyl arsine oxide they obtained p-tolyl phenyl arsenious oxide ($p\text{-}C_7H_7.PhAs)_2O$. This also affords a ready method of preparing asymmetric tertiary arsines. If diphenyl chloroarsine be treated with a solution of potassium cyanide, the chlorine atom is replaced by the cyanogen group giving diphenyl cyano arsine. Both of these compounds were used as sternutators by the Germans during the world war. They are both solids, the chloro compound melting at $45°$ when pure (generally below $40°$ C.), and the cyano compound at $31°$ C. They were dispersed in the form of fine dust by heavy explosive charges, the clouds lasting only a short time. Fortunately for the Allies the German technique in this case was at fault, as the dispersal of the arsine was on the whole a failure. Diphenyl chloroarsine is hydrolysed slowly in moist air. It is stated to be effective at concentrations as

low as 1 part in 25,000,000. It is immediately effective and readily penetrated the existing masks of the Allies. Diphenyl cyanoarsine was used by the Germans in May, 1918. It is more stable towards water than the chloro compound, and also more irritant, being effective at concentrations as low as 1 part in 50,000,000. Phenyl dichloroarsine (b.pt. 252° C.) was used by the Germans in 1917–18 and also by the Allies. It is a lung irritant and

$$As\ (ONa)_3 \xrightarrow[\;SO_2+HI\;]{\;Ph\ N_2\ Cl.\;} Ph\ \overset{O}{As}\ (ONa)_2$$

$$Ph\ As\ Cl_2 \xleftarrow{\quad NaOH \quad} Ph\ As\ (ONa)_2$$

$$\xleftarrow{R\ N_2\ Cl} \qquad\qquad \downarrow Me\ I$$

$$Ph\ R\ \overset{O}{As}\ (OH) \qquad Ph\ Me\ \overset{O}{As}\ (OH)$$

$$\downarrow SO_2 \qquad\qquad\qquad \downarrow HI$$

$$Ph\ R\ As\ Cl \qquad\qquad Ph\ Me\ As\ I$$

$$\downarrow Grignard \qquad\qquad \downarrow Grignard$$

$$Ph\ R\ R'\ As \qquad\qquad Ph\ Me\ R.\ As$$

$$Ph\ R.\ As\ CN \qquad\qquad Ph\ Me\ R.\ As{:}O$$
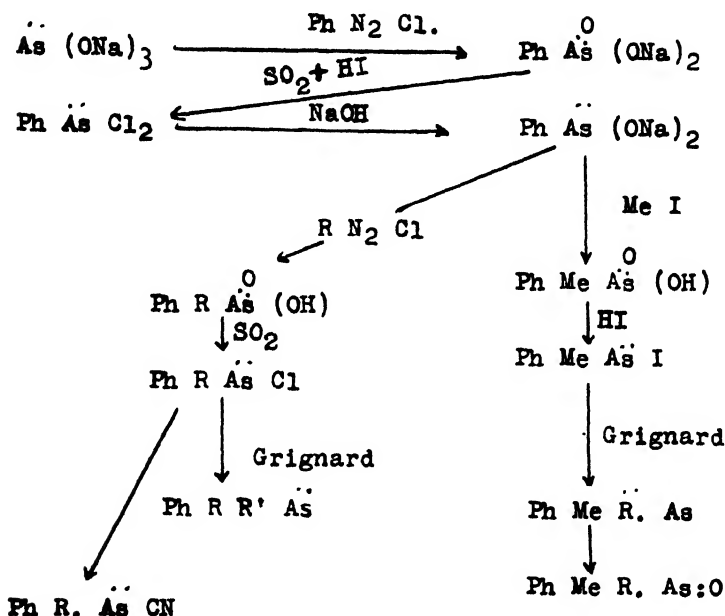
Fig. 2

also a vesicant and sternutator. A concentration of 0·26 mg. per litre is fatal in 10 minutes. It is hydrolysed in water and is easily oxidised. Actually it was not used to any great extent in the last war, being used mainly as a solvent for diphenyl chloroarsine. The corresponding bromo compound, $PhAsBr_2$, was the last lung irritant introduced during the World War, and there is very little record of its effects. It is claimed that 0·020 mg. per litre will prove fatal in 10 minutes. Its toxicity exceeds that of any other lung irritant used.

Tertiary arsines are readily oxidised by oxidising agents (e.g. hydrogen peroxide), to arsine oxides of the type R_3AsO. It was found, however, that on exposure to moist air, phenyl dimethyl arsine and p-tolyl dimethyl arsine were both slowly oxidised to arsinic acids, with the loss of a methyl group (presumably as methyl alcohol).[27]

$$PhAsMe_2 + H_2O + O_2 = PhMeAs.O.OH + MeOH.$$
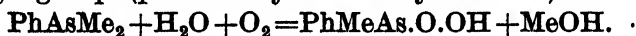
This reaction could be accelerated by bubbling oxygen through the arsine in the presence of water.

It was later found that p-tolyl methyl dihydroxy arsonium chloride and p-tolyl methyl arsinic acid could be demethylated by lead tetrachloride, yielding p-tolyl arsonic acid.[28]

$$PhMeAsO.OH \rightarrow PhAsO(OH)_2.$$
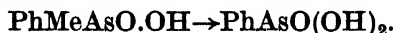
Arsine oxides and arsinic acids possess basic properties to the extent that they will combine with acids to give hydroxy salts, e.g.

$$PhMeAsO.OH \rightarrow PhMeAsO.OH.HCl$$
$$PhMe_2AsO \rightarrow PhMe_2As.O.HCl.$$
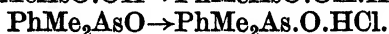
Both types are soluble in water, acetone, and alcohol, and give acid reactions. The aqueous solutions may be titrated (quantitatively) with barium hydroxide solution. The formulæ assigned to them, viz. $(PhMe_2AsOH)Cl$ and $(PhMeAs(OH)_2)Cl$,[29] are consistent with their reactions in solution. Thus the hydroxy nitrate and hydroxy sulphate may be prepared by treating the hydroxy chloride with the calculated amount of silver nitrate or sulphate. The acid reaction in aqueous solution must be attributed to secondary dissociation of the complex ion. It is rather remarkable that some of these hydroxy salts are also soluble in chloroform and can be obtained in the pure form by recrystallisation from this solvent. Presumably they break down into their original components in hot chloroform, and, on cooling, recombine and separate in the crystalline form.

It is interesting to note that diphenyl methyl arsine dichloride is soluble in water, giving an acid reaction due no doubt to hydrolysis to the hydroxy chloride and hydrochloric acid. It is also soluble, however, in benzene, and the molecular weight, determined by the cryoscopic method, in this solvent (317) agrees very closely with that calculated from the formula $Ph_2MeAsCl_2$ (315).[30] This result indicates definitely that in benzene solution the compound is not split up into simpler molecules. This

raises the question of the valency of the arsenic atom, and the mode of attachment of the chlorine in this type of compound. It is obvious that further experimental work should be carried out with arsine dihalides, dihydroxides, and hydroxy salts.

Hydroxy salts formed from asymmetric tertiary arsines (e.g. phenyl α naphthyl methyl arsine) and d-bromo camphor sulphonic acid have been obtained, and attempts made to separate the two optically active forms by fractional crystallisation, but without success.

(4) *Friedel and Kraft Reaction.*

Prior to 1921, it had been considered that the Friedel and Kraft reaction was not generally applicable to chloroarsines. In that year, however, it was shown that not only was triphenyl arsine formed from diphenyl chloroarsine and benzene in the presence of aluminium chloride, but also that in carbon disulphide solution, aluminium chloride converted γ phenyl-propyl ethyl chloroarsine into the cyclic compound As-methyl tetrahydro arsinoline.[31] Two years later Wieland[32] found that the Friedel and Kraft reaction could be used for the production of primary, secondary and tertiary arsines. As a result of this we now have a simple method of preparing triphenylarsine, by the action of arsenious chloride on benzene in the presence of aluminium chloride. As triphenyl arsine can be easily degraded to diphenyl chloroarsine by treatment with arsenious chloride, it would appear that this will be the most satisfactory method of producing diphenyl chloroarsine in quantity in the event of this compound being required for war purposes.

Heating secondary aromatic amines with arsenious chloride gives rise to the phenarsazines.[33] For example, when diphenylamine is heated under reflux with arsenious chloride, the product is 10-chloro-5·10-dihydro phenarsazine (Fig. 3A). Actually this compound was prepared in Britain and America for use in the last war and is referred to in the literature as diphenyl amine chloro arsine. It is a powerful sternutator. It is a yellow to green solid with a m.pt. of 195° C., insoluble in water and only very slowly hydrolysed in moist air. Its effective concentration is given as 1 in 30,000,000. It is far more easily and cheaply manufactured than diphenyl chloroarsine and is stated to be at least just as effective. Apparently, production came too late for use in the last war. Quite

a number of phenarsazines have been prepared by using other secondary amines and their substitution products. By heating diphenyl amine with β chlorovinyl dichloroarsine β chlorovinyl phenarsazine is obtained[34] (Fig. 3D).

(A)

(B)

(C)

(D)   Fig. 3   (E)
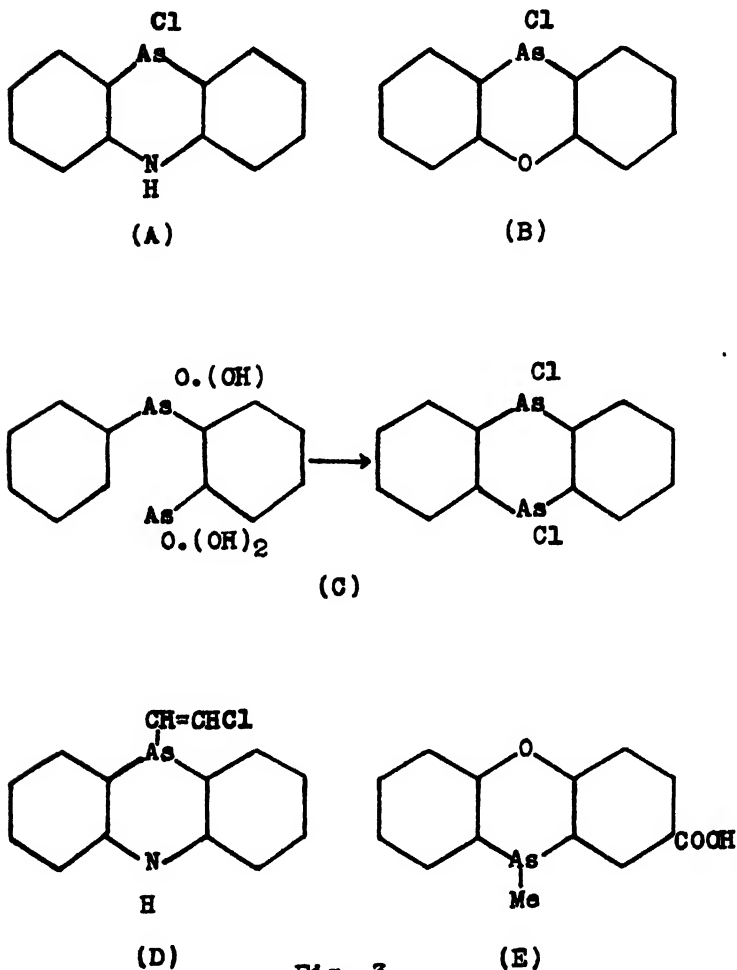
The chlorine atom in these compounds is reactive. The chloroarsine may be oxidised to the corresponding arsonic acid, or it may be coupled with a Grignard reagent to give an arsine.[35]

In a similar manner, aryl ethers react with arsenious chloride on heating and in this case aluminium chloride is used as catalyst.[36] Thus diphenyl ether and arsenious chloride yield 5-chloro phenoxarsine (Fig. 3B). A phenoxarsine of particular interest is 3-carboxy 5 methyl phenoxarsine, obtained in optically active form by Turner and Lesslie[37] (Fig. 3E). Arsanthrene chloride (Fig. 3C) is prepared by passing a current of sulphur dioxide into a hydrochloric acid solution of diphenyl arsinic o-arsonic acid to which a little potassium iodide has been added, and then distilling.[38]

Phenols and primary amines may be directly arsonated by heating with arsenic acid, yielding p-hydroxy[39] or (amino)[40] phenylarsonic acid.

Fig. 4 illustrates a few of the methods now available for the preparation of 3-amino 4-hydroxy phenyl arsonic acid,[41] a compound which may easily be converted into several arsenicals of great therapeutic importance. A few of the methods of preparation are as follows :

(1) Aniline $\xrightarrow{\text{Bart}}$ phenylarsonic acid→p nitro phenyl arsonic acid.
    p-amino phenyl arsonic acid→4 amino 3 nitro phenyl arsonic acid→4 hydroxy 3 amino phenyl arsonic acid.

(2) Aniline $\xrightarrow{\text{H}_3\text{AsO}_4}$ p amino phenyl arsonic acid→p hydroxy phenyl arsonic acid→4 hydroxy 3-amino phenyl arsonic acid.

(3) p-chloroaniline → p-chlorophenylarsonic acid → 3 nitro 4 chlorophenylarsonic acid→3 nitro 4 hydroxy phenyl arsonic acid→3 amino 4 hydroxy phenyl arsonic acid.

(4) p-nitraniline→p-nitro phenyl arsonic acid→p-amino phenyl arsonic acid→3 nitro 4 amino phenyl arsonic acid→3 nitro 4 hydroxy phenyl arsonic acid→3 amino 4-hydroxy phenyl arsonic acid.

(5) Phenol $\xrightarrow{\text{H}_3\text{AsO}_4}$ p-hydroxy phenyl arsonic acid→3 nitro 4 hydroxy phenyl arsonic acid→3 amino 4 hydroxy phenyl arsonic acid.

(6) Aniline $\xrightarrow{H_3AsO_4}$ p-amino phenyl arsonic acid →
diazonium compound $\xrightarrow{(HCl \ and \ Cu)}$ p-chlor phenyl
arsonic acid → 3 nitro 4-chloro phenyl arsonic
acid $\xrightarrow{KOH}$ 3 nitro 4-hydroxy phenyl arsonic
acid → 3 amino 4 hydroxy phenyl arsonic acid.
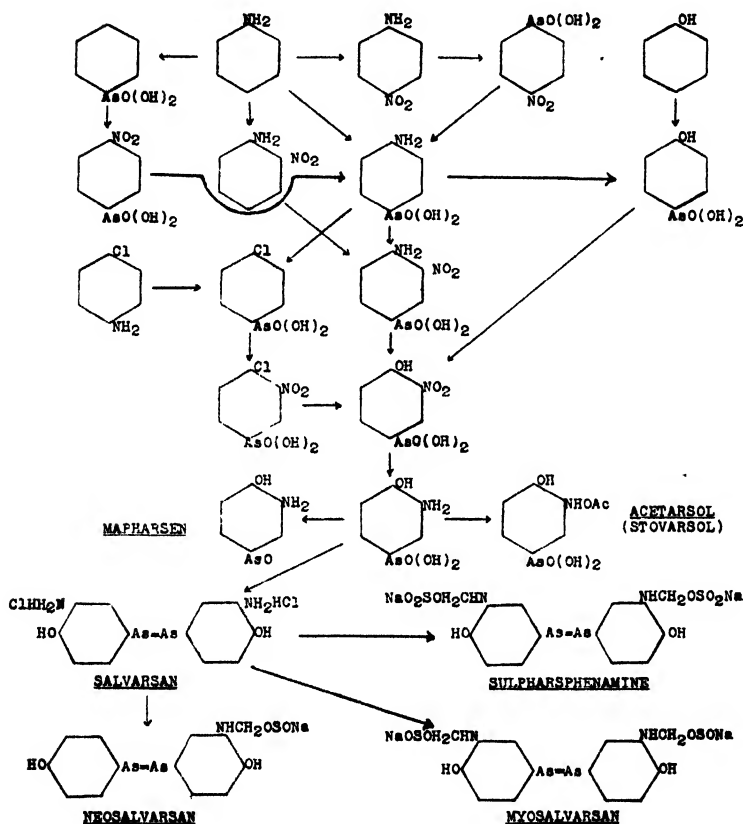
FIG. 4.

3 amino 4 hydroxy phenyl arsonic acid is converted into
the following drugs :

   (a) *Mapharsen* by reducing the arsonic acid to oxide
      with sulphur dioxide in the usual way.

   (b) *Acetarsol* (*stovarsol*) by acetylation.[42]

(c) *Salvarsan* (*arsphenamine*) by reducing the arsonic acid with hypophosphorus acid (in presence of hydriodic acid).[43]

(d) *Neosalvarsan* (*neoarsphenamine*) by the action of sodium formaldehyde sulphoxylate on salvarsan.[44]

(e) *Sulpharsphenamine* by the action of formaldehyde and sodium bisulphite on salvarsan.[45]

The preparation of 3-amino 4 hydroxy phenyl arsonic acid is represented diagrammatically in Fig. 4.

In conclusion, I would like to refer to the stability of 4-covalent derivatives of arsenic.

An outstanding property of the arsenic atom is the readiness with which it passes from the tervalent to the 4-covalent state. This is shown by the ease with which sodium arsenite or sodium phenyl arsenite may be alkylated or arylated as in the Meyer and Bart reactions. It is also shown by the readiness with which a tertiary arsine combines with methyl iodide to give a quaternary arsonium iodide. These reactions are of course associated with the lone pair of electrons present in tervalent arsenic.

For the same reason tertiary arsines are found to coordinate with metallic salts, and during the past few years compounds of this type have been described with salts of silver,[46] platinum,[47] mercury.[48] copper,[49] cadmium[50] and zinc,[51] the number of molecules of the arsine to one of the salt being either one or two. In many cases these compounds were found to be quite stable. In others it was impossible to recrystallise the compound without losing arsine. In exceptional cases the compounds could not even be washed with cold ether or benzene without loss of arsine. This result would indicate that the co-ordinate link in some of these compounds is weak, a fact which is well illustrated by the behaviour of certain compounds of tertiary arsines with compounds such as methyl diiodo arsine described some years ago.[52] Although these compounds crystallised well from alcohol or acetone and gave sharp characteristic melting points, yet in benzene solution their molecular weights indicated that they were completely broken down again into the original components. This result was confirmed by adding methyl iodide to such a solution in benzene. The arsine was recovered quantitatively as methiodide.

Compounds formed with salts of silver, platinum and copper were found generally to be quite stable. One compound prepared from cupric chloride and diphenyl

methyl arsine is of particular interest.   It is quite stable, its composition agreeing with the empirical formula $Cu_2Cl_3(Ph_2AsMe)_3$.   The compound is readily prepared in two isomeric forms, one of which is brown and the other blue.   They have the same molecular weight and melt at the same temperature.   The blue form slowly changes to the brown in the solid state or more rapidly on heating in nitrobenzene.   Under the right conditions the two forms separate simultaneously from solution.   In both forms one of the copper atoms is in the cuprous condition, the other being cupric.   Certain alternative formulæ which would account for the isomerism were suggested when the compounds were first described.   Since then it has been shown that the following formulæ are more consistent with the accepted views of the stereochemistry of cuprous and cupric complexes.[53]
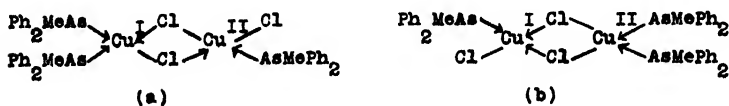
Fig.5.

Both Cu^I and Cu^{II} are 4-covalent, the former having a tetrahedral and the latter a planar configuration.

Coordination compounds have been prepared by the action of asymmetric tertiary arsines (such as phenyl α naphthyl methyl arsine and p-tolyl methyl ethyl arsine) and the copper and silver salts of d-bromo camphor sulphonic acid.   In each of these compounds the arsenic atom should function as a centre of asymmetry, and if the coordinate link is a true covalent bond it was thought, that by fractional crystallisation, evidence of the existence of different optically active forms would be obtained.   So far, however, these attempts have not met with any success.

The behaviour of arsonium iodides also is frequently abnormal.   Thus if phenyl methyl ethyl arsine is treated with methyl iodide the product obtained under all conditions is found to be phenyl dimethyl ethyl arsonium iodide melting at 142° C.   But if phenyl dimethyl arsine is treated with ethyl iodide, instead of always obtaining the same arsonium iodide as before, mixtures are obtained varying in composition and melting point according to the conditions.[54]

This result would indicate that the quaternary arsonium iodide when formed, has a tendency to split up again into tertiary arsine and alkyl iodide—in other words, there is a state of equilibrium between tervalent arsine and 4-covalent arsonium iodide : $R_4AsI \rightleftharpoons R_3As + RI$.

In this respect, these arsonium ions differ from their ammonium and phosphonium analogues. This, no doubt explains why, so far, no asymmetric arsine oxide has been resolved into optically active forms although Meisenheimer apparently had little difficulty in resolving phosphine and amine oxides. It also explains the difficulty of resolving simple quaternary arsonium ions. The only optically active salt of this type so far described is d-phenyl α naphthyl benzyl methyl arsonium iodide,[55] and even this could be prepared with only a small rotation and was found to racemise quickly. On the other hand Mills and Raper[56] had no difficulty in resolving p-carboxy phenyl methyl ethyl arsine sulphide $p\text{-}C_6H_4 {<}^{COOH}_{\phantom{<}S} AsMeEt$,

$MeEtAsC_6H_4COOH$, and found the active forms to be optically stable. In this compound there is no possibility of a change of valency of the arsenic atom.

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[9] Burrows and Turner : *J.C.S.*, 1920, *117*, 1376.
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[11] Burrows and Turner : *Loc. cit.*
[12] Steinkopf and Schwen : *Ber.*, 1921, *54* (*B*), 1454.
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[15] Palmer : *Ber.*, 1894, *27*, 1378. Dehn and Wilcox : *Am. Chem. J.*, 1906, *35*, 1.
[16] Dafert : *Monat.*, 1919, *40*, 313.
[17] Green and Price : *J.C.S.*, 1921, *119*, 448. Mann and Pope : *Ibid.*, 1922, *121*, 1754. Lewis and Stiegler : *J.A.C.S.*, 1925, *47*, 2546.
[18] Burrows and Turner : *J.C.S.*, 1920, *117*, 1382.

[19] Brit. Pat., 1918 (142880). Pope and Turner : *J.C.S.*, 1920, *117*, 1450. Morgan and Vining : *Ibid.*, 1920, *117*, 780.

[20] Michaelis : *Ann.*, 1902, *321*, 211, 226. Michaelis and Paetow: *Ber.*, 1885, *18*, 41. Michaelis and Weitz : *Ibid.*, 1887, *20*, 49.

[21] Bart : German Pat., 1912 (250264), (254092).

[22] Brit. Pat., 1919 (142947). Schmidt : *Ann.*, 1920, *42*, 159.

[23] Bart : *Ann.*, 1922, *429*, 100.

[24] Burrows and Turner : *J.C.S.*, 1920, *117*, 1373 ; 1921, *119*, 426.

[25] Burrows and Turner : *Loc. cit.*

[26] Blicke and Smith : *J.A.C.S.*, 1929, *51*, 3479.

[27] Burrows : *Proc. Roy. Soc. N.S.W.*, 1935, *68*, 72.

[28] Burrows and Lench : *Ibid.*, 1937, *70*, 295.

[29] Burrows : *Loc. cit.*

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[31] Burrows and Turner : *J.C.S.*, 1921, *119*, 426.

[32] Wieland : *Ann.*, 1923, *431*, 30.

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[35] Aeschlimaru: *J.C.S.*, 1927, p. 414.

[36] Lewis, Lowry and Bergein : *J. Am. Chem. Soc.*, 1921, *43*, 890. Turner and Sheppard : *J.C.S.*, 1925, *127*, 544.

[37] Turner and Lesslie : *J.C.S.*, 1934, 1170 ; 1935, 1150, 1268.

[38] Kalb : *Ann.*, 1921, *423*, 39.

[39] Hamilton and Johnston : *J. Am. Chem. Soc.*, 1926, *48*, 1406. Conant : *Ibid.*, 1919, *41*, 431. Jacobs and Heidelberger : *Ibid.*, 1440.

[40] Cheetham and Smith : *J. Am. Chem. Soc.*, 1920, *42*, 828.

[41] Benda and Bertheim : *Ber.*, 1911, *44*, 3445 ; *J. Am. Chem. Soc.*, 1919, *41*, 431. Bart : *Ann.*, 1922, *429*, 98. Karrer : *Ber.*, 1913, *46*, 515. Ismailski and Siminow : *Journ. de Pharm. et de Chem.*, *22*, 345.

[42] Raiziss and Gavron : *J. Am. Chem. Soc.*, 1921, *43*, 583.

[43] Bart : *Ann.*, 1922, *429*, 113. Ehrlich and Bertheim : *Ber.*, 1912, *45*, 756. Fargher and Pyman : *J.C.S.*, 1920, *117*, 376, Christiansen : *J. Am. Chem. Soc.*, 1920, *42*, 2402 ; 1921. *43*, 370.

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[46] Burrows and Parker : *J. Am. Chem. Soc.*, 1933, *55*, 4133.

[47] Burrows and Parker : *Proc. Roy. Soc. N.S.W.*, 1934. *68*, 39.

[48] Anderson and Burrows : *Ibid.*, 1936, *70*, 63.

[49] Burrows and Sanford : *Ibid.*, 1935, *69*, 182.

[50] Burrows and Lench : *Ibid.*, 1936, *70*, 218.

[51] Burrows and Lench : *Ibid.*, 1936, *70*, 222.

[52] Burrows and Turner : *J.C.S.*, 1920, *117*, 1373.

[53] Mellor, Morris and Burrows : *Nature*, 1938, *141*, 414.

[54] Burrows and Turner : *J.C.S.*, 1921, *119*, 436.

[55] Burrows and Turner : *Loc. cit.*

[56] Mills and Raper : *J.C.S.*, 1925, *127*, 2479.

ABSTRACT OF PROCEEDINGS

OF THE

Royal Society of New South Wales

April 3, 1940.

The Annual Meeting, being the five hundred and seventy-sixth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

Dr. H. S. Halcro Wardlaw, President, was in the chair. Sixty members and two visitors were present. The minutes of the general monthly meeting of December 6th, 1939, were read and confirmed.

The President announced the deaths of Major L. A. Curtis, a member since 1912, and of Sir Hubert Murray, an Honorary Member since 1935.

The following gentlemen were elected officers and members of the Council for the coming year:

President:

PROF. A. P. ELKIN, M.A., Ph.D.

Vice-Presidents:

H. S. HALCRO WARDLAW, D.Sc., F.A.C.I.

PROF. J. C. EARL, D.Sc., Ph.D.

W. L. WATERHOUSE, M.C., D.Sc.Agr., D.I.C., F.L.S.

E. H. BOOTH, M.C., D.Sc., F.Inst.P.

Honorary Secretaries:

A. R. PENFOLD, F.A.C.I., F.C.S. | C. ANDERSON, M.A., D.Sc.

Honorary Treasurer:

M. B. WELCH, B.Sc., A.I.C.

Members of Council:

PROF. V. A. BAILEY, M.A., D.Phil., F.Inst.P.

A. BOLLIGER, Ph.D., A.A.C.I.

W. R. BROWNE, D.Sc.

A. CLUNIES ROSS, B.Sc., F.C.A. (Aust.)

PROF. L. A. COTTON, M.A., D.Sc.

PROF. C. E. FAWSITT, D.Sc., Ph.D.

E. J. KENNY, M.Aust.I.M.M.

D. P. MELLOR, M.Sc.

H. G. RAGGATT, D.Sc.*

PROF. T. G. ROOM, M.A.

A. B. WALKOM, D.Sc.†

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* Resigned June 26, 1940.

† Elected July 31, 1940.

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Treasurer, and on the motion of Mr. Welch, seconded by Mr. A. D. Ollé, were adopted.

THE ROYAL SOCIETY OF NEW SOUTH WALES.
BALANCE SHEET AS AT 29th FEBRUARY, 1940.

LIABILITIES.

1939. £		£ s. d.	£ s. d.	£ s. d.
	Trust Funds—			
	Clarke Memorial Fund—			
	Balance as at 28th February, 1939	1,689 1 9		
	Add Interest for year ended 29th February, 1940	67 11 3		
		£1,756 13 0		
	Less Expenses in connection with 1939 Lecture and Medal—			
	Lecture Fee £26 5 0			
	Printing 13 8 11			
	Advertising 0 15 0			
	Engraving 0 9 6			
		40 18 5	1,715 14 7	
	Walter Burfitt Prize Fund—			
	Balance as at 28th February, 1939	636 8 8		
	Add Interest for year ended 29th February, 1940	25 9 1		
			661 17 9	
	Liversidge Bequest—			
	Balance as at 28th February, 1939	676 8 7		
	Add Interest for year ended 29th February, 1940	27 1 1		
			703 9 8	
3,002				3,081 2 0
6	Subscriptions Paid in Advance			10 10 0
	Provision for Unexpired Proportion of Life Membership			
167	Subscriptions			156 0 0
26,669	Accumulated Fund			26,685 15 1
£29,844				£29,933 7 1

ASSETS.

1939. £		1940. £ s. d.	£ s. d.
	Cash at Bank and on Hand—		
	The Union Bank of Australia Ltd.	90 17 2	
	Commonwealth Savings Bank of Australia	119 15 2	
399	Petty Cash..	3 0 1	213 12 5
	Bonds and Inscribed Stock—		
	Bonds (Face Value £1,000)	1,011 5 0	
7,539	Stock (Face Value £6,860)	6,827 11 3	7,838 16 3
	Science House Management Committee—		
14,590	Payments to date		14,590 0 0
	Sundry Debtors—		
	Subscriptions Unpaid	332 8 10	
	Less Reserve	332 8 10	
6,800	Library ..		6,800 0 0
	Furniture	433 1 1	
433	*Less* Depreciation written off	21 13 0	411 8 1
	Pictures	46 1 8	
46	*Less* Depreciation written off	2 6 0	43 15 8
	Microscopes	20 8 8	
20	*Less* Depreciation written off	1 0 0	19 8 8
	Lantern ..	17 3 0	
17	*Less* Depreciation written off	0 17 0	16 6 0
£29,844			£29,933 7 1

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 29th February, 1940, as disclosed thereby. We have obtained certificates showing that the whole of the Bonds and Inscribed Stock are held by the Society's bankers for safe keeping.
National Mutual Building,

350 George Street,   HORLEY & HORLEY,
  Sydney, 18th March, 1940.   Chartered Accountants (Aust.).

REVENUE ACCOUNT FOR THE YEAR ENDED
29th FEBRUARY, 1940.

Period ended 28th Feb., 1939. £	£						Year ended 29th February, 1940. £ s. d.	£ s. d.
	3	To Advertising	..	..	..	..	3 16 3	
	34	,, Cleaning	..	..	..	..	29 17 6	
	24	,, Depreciation	..	..	..	..	25 16 0	
	5	,, Electric Light and Gas	..	..	..	6 2 9	
	14	,, Insurance	..	..	..	..	13 19 1	
	60	,, Library Maintenance	..	..	..	77 5 9	
	53	,, Miscellaneous Expenses	..	..	..	56 3 7	
	236	,, Office Salaries and Audit Fees	..	..	259 7 0	
	9	,, Office Sundries and Stationery	..	..	29 6 8	
	165	,, Printing	..	..	..	..	118 19 8	
	451	,, Printing and Publishing Journal	..	..	272 17 3	
	5	,, Repairs	..	..	..	..	6 4 6	
	52	,, Stamps and Telegrams	..	..	..	49 0 8	
	11	,, Telephone	..	..	..	..	16 9 10	
		,, Annual Dinner—						
49		Expenses	..	..	£55 4 4			
34	15	*Less* Received	..	..	40 19 0			
							14 5 4	
£1,137								979 11 10
	90	,, Balance, being Net Revenue for the Year, transferred to Accumulated Fund	..	..	..		50 0 5
£1,227								£1,029 12 3

Period ended 23th Feb., 1939. £	£						Year ended 29th February, 1940. £ s. d.	£ s. d.
	488	By Members' Subscriptions	..	..	..		475 13 0
	400	,, Government Subsidy	..	..	..		0 0 0
109		,, Science House Receipts	..	..	..	260 0 0	
39		*Less* Rent Paid	..	..	..	15 9 8	
	70							244 10 4
	103	,, Miscellaneous Receipts	..	..	..		100 1 0
247		,, Interest Received	..	..	..	297 9 4	
		Less—						
			Clarke Memorial Fund	£67 11 3				
			Walter Burfitt Prize Fund	25 9 1				
111			Liversidge Bequest	27 1 1				
	136					120 1 5		
								177 7 11
	30	,, Proportion of Life Members' Subscriptions					32 0 0
£1,227								£1,029 12 3

ACCUMULATED FUND ACCOUNT FOR THE YEAR ENDED
29th FEBRUARY, 1940.

	£ s. d.
1940—February 29—	
To Arrears of Subscriptions, written off	9 9 0
,, Amount transferred to Bad Debts Reserve Account ..	24 7 10
,, Balance Carried Down	26,685 15 1
	£26,719 11 11

	£ s. d.
1939—February 28—	
By Balance from last Account	26,669 11 6
1940—February 29—	
By Net Revenue for the Year	50 0 5
	£26,719 11 11
1940—February 29—	
By Balance Brought Down	£26,685 15 1

The Annual Report of the Council (1939-1940) was read, and on the motion of Mr. Sussmilch, seconded by Mr. Challinor, was adopted.

REPORT OF THE COUNCIL (RULE XXVI), 1939-1940.

We regret to report that we have lost by death eight members : His Honour Judge A. P. Backhouse (elected 1878), Mr. Samuel Cornwell (1882), Major L. A. Curtis (1912), Mr. W. W. L'Estrange (1916), Sir John Hubert Plunkett Murray (Hon. Member, 1935), Dr. Harvey Nickoll (1924), Rev. Father W. J. O'Leary (1930), and Mr. Wilfred J. Spruson (1917).

By resignation we have lost eight members : G. H. Abbott, John Andrews, Sidney Willis England, A. T. Keeble, Harold G. McQuiggin, Arthur Cyril Weeks Mears, Keith E. W. Salter, Cyrus W. O. Tye.

Nine ordinary members were elected during the year : Elizabeth Marie Basnett, George Gascoigne Blake, Richard Charles Leslie Bosworth, Norman Augustus Faull, Robert Mortimer Gascoigne, Arthur James Lambeth, Allan Maccoll, Ernest Ritchie, Alice Victoria May Thomas.

Mr. Frederick Chapman, of Melbourne, was elected an Honorary Member.

The membership of the Society as at the end of March stands at seven honorary members and two hundred and sixty ordinary members.

During the year beginning April 1st, there have been nine general monthly meetings and ten meetings of the Council. The average attendance at the general meetings was twenty-five, and at the Council meetings thirteen.

Twenty-two papers were read during the year under review. The following short talks were delivered :

"Experiences in the U.S.A. and Great Britain ", by Mr. D. P. Mellor.

"Biological Erosion of Gas Mains ", by Mr. F. G. Pont.

"Distribution of Oil Supplies ", by Dr. H. G. Raggatt.

"Coloration of Animals ", by Mr. A. S. Le Souef.

"The Sixth Pacific Science Congress ", by Mr. E. C. Andrews.

"Artificial Radio-Activity ", by F. L. Arnot.

"An Expedition amongst the Natives of Central and East Africa ", by Dr. W. E. H. Stanner.

Exhibits were shown at meetings by Professor Vonwiller, Dr. A. Bolliger, Mr. D. P. Mellor, and Mr. M. R. Freney.

Five Popular Science Lectures were given during the winter season, and were well attended by members of the Society and also by the general public :

June 21st.—" Cold Light ", by D. P. Mellor, M.Sc.

July 20th.—" Whaling ", by Professor W. J. Dakin, D.Sc., F.L.S., F.Z.S.

August 31st.—" The Living Soil ", by J. M. Vincent, B.Sc.Agr.

September 21st.—" Nature and Nurture ", by Professor Eric Ashby, D.Sc., D.I.C., F.L.S.

October 19th.—" How Nerves Work ", by Dr. J. C. Eccles, M.B., B.Sc. (Melb.), M.A., D.Phil. (Oxon), F.R.A.C.P.

The Annual Dinner was held on March 28th at the Union Refectory at the University of Sydney. The guest of honour was Sir Ernest Fisk, K.B., F.Inst.R.E., A.M.I.E.(Aust.), and the Minister for Education (the Hon. D. H. Drummond) and the Lord Mayor of Sydney, Mr.

Stanley Crick, were among the guests. Sixty-eight persons were present.

National Emergency Committee.—Early in the year a committee was formed consisting of the executive officers, together with Professor Cotton, Mr. Challinor, Professor Vonwiller, Professor Fawsitt, and Dr. W. L. Waterhouse, with the object of formulating a policy for the Royal Society, to make effective its offer of assistance to the Government in the event of a national emergency.

Conversazione.—A Conversazione, to be held in December, was arranged, and His Excellency the Governor, the Lord Wakehurst, had consented to be present, but on the outbreak of war he intimated his inability to attend, and it was decided to postpone the function indefinitely.

The Clarke Memorial Lecture was delivered by Sir John Flett, and was very well attended.

The Clarke Memorial Medal was awarded to Mr. C. A. Sussmilch for his researches in geology.

Government Grant.—During 1939 the Government grant of £400 was received by the Society.

Science House.—Meetings of the Science House Management Committee had been held regularly. The Royal Society has been represented on the committee by Mr. E. Cheel and Mr. M. B. Welch, with Dr. C. Anderson and Dr. H. S. Halcro Wardlaw as substitute members.

Publication of Journal and Proceedings.—During the year 1939 the resolution of July, 1938, that the Journal and Proceedings be published in four quarterly parts was carried into effect, and the Journal has appeared on June 1st, September 1st, and December 1st, the last number being due on March 1st.

Mr. D. P. Mellor was appointed to assist Dr. C. Anderson in the work of editing the Journal and Proceedings.

Finance Committee.—A Finance Committee consisting of the executive officers, with Mr. Cheel and Mr. Allan Clunies Ross was appointed to advise the Council regarding its investments.

Professor Millikan's Visit.—During his visit to Sydney, Professor Millikan, the well known authority on cosmic rays, was entertained by the Royal Society and the Australian National Research Council at an afternoon tea in the Royal Society's rooms.

The Library.

The Council accepted with regret the resignation of Mr. H. Williams from the office of Honorary Librarian, owing to his departure for England. Professor J. C. Earl was appointed Honorary Librarian.

Maps.—At the suggestion of Professor Earl and Professor Macdonald Holmes, Mr. W. H. Maze was asked and agreed to go through a number of maps and charts which are uncatalogued in the library. Mr. Maze reported that for the most part the maps were in a very bad state of repair, and that in his opinion the few maps which are of value do not warrant the expense of installing map cabinets. He stated that there were a number of geological maps which might be of some value, and suggested that a geologist be asked to report on them. There were also maps which might be of value to geographers, and a certain number of maps and charts of historical value, including plans for the alteration of the Royal Society's premises in Elizabeth Street, Sydney.

Purchase of Periodicals, and, Bookbinding.—The amount of £26 0s. 6d. has been expended on the purchase of periodicals during the year. A number of periodicals have been bound, at a cost of £46 14s. 3d. The total cost of periodicals and binding amounts to £72 14s. 9d.

Exchanges.—The total number of societies and institutions with which publications are exchanged is at present 319.´ Owing to the war, exchanges from 6 Austrian, 3 Czechoslovakian and 33 German institutions have been suspended temporarily. It is understood, however, that some action is contemplated in the direction of ensuring continuity in the receipt of important foreign periodicals of a scientific nature from countries with which we are at war.

Accessions.—For the twelve months ended February 29th, 1940, the number of accessions entered in the Catalogue is 3,030 parts of periodicals, 251 whole numbers, and 91 back numbers, which helped to complete sets.

Borrowers and Readers.—The number of readers' tickets issued to the Australian Chemical Institute annually is 25, but a very small number of the members of the Institute avail themselves of the privilege of reading.

The readers visiting the library during the year numbered 12, and the number of books and periodicals borrowed by institutions, members, and accredited readers has been 61. Among the institutions which have borrowed books are the University of Sydney, University of Western Australia, the C.S.I.R. (Divisions of Plant Industry, Economic Entomology), the McMaster Laboratory, the Royal Society of Tasmania, the Commonwealth Solar Observatory, Canberra, the Commonwealth Forestry Commission, and the Irrigation Commission.

The Honorary Librarian would again draw attention to the congested state of the small and large storerooms, and to the recommendations placed before the Council in the Library Committee's report of 1936, namely that shelving twelve inches deep be fitted to the west wall of the large storeroom, to hold the stock of journals, which are at present nailed up in packing cases and almost inaccessible.

H. S. HALCRO WARDLAW,
President.

The following donations were received : 749 parts of periodicals, and 50 whole volumes.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificate of one candidate for admission as an ordinary member of the Society was read for the second time, and William Dudgeon was duly elected an ordinary member of the Society.

The President, Dr. H. S. Halcro Wardlaw, then delivered his address, entitled " Some Features of the Exchange of Energy between Man and his Environment ".

Dr. H. S. Halcro Wardlaw, the retiring President, then installed Professor A. P. Elkin as President for the year 1940-1941, and the latter expressed his thanks and his pleasure on taking office. On behalf of the members Professor Fawsitt expressed appreciation of the work and the address of the retiring President. Dr. Wardlaw briefly replied, expressing thanks for the help and cooperation he had received from his colleagues on the Council.

The following papers were read by title only :

" Studies on the Tung Oil Tree (*Aleurites Fordii* Hemsl.)." Part I. By S. Smith-White, B.Sc.Agr. (Communicated by A. R. Penfold, F.A.C.I., F.C.S.)

" The Reduction of Some Aromatic Nitro-Compounds by Hydrogen and Raney-Nickel at Atmospheric Temperature and Pressure", by A. Albert, B.Sc., Ph.D., and B. Ritchie, B.Sc.

" Substituted Indenes." Part I. By V. M. Trikojus, B.Sc., D.Phil., and D. E. White, M.Sc., D.Phil.

May 1, 1940.

The five hundred and seventy-seventh General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Professor A. P. Elkin, President, was in the chair. Twenty-eight members and two visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificates of sixteen candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Reginald Frank Cane and Frederick Noel Hanlon.

The President announced that the Clarke Memorial Lecture would be delivered by Mr. E. J. Kenny, and would be entitled " The Geologist and Sub-surface Water ".

Section of Physics.—The Section of Physics notified the Council that the Section was to be dissolved, owing to the formation of a New South Wales Division of the Institute of Physics.

The following donations were received : 215 parts of periodicals, and 20 whole volumes.

Notice of Motion.—The President gave notice of motion for the next general meeting with regard to a proposed alteration of Rule VIII.

The following paper was read :

" Structural Geology of the Mudgee-Gunnedah Region ", by J. A. Dulhunty, B.Sc.

June 5, 1940.

The five hundred and seventy-eighth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Professor A. P. Elkin, President, was in the chair. Forty members and two visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificates of twenty-eight candidates for admission as ordinary members of the Society were read for the first time.

The certificates of sixteen candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Robert Cecil Betty, Arthur Charles Allenby Flack, Martin Raphael Freney, Richard Galvin Gillis, Thomas William Heselton, Menzie Lipson, William Hutton Lockwood, Edgar Howard Mercer, James Edward Mills, Benjamin Sydney Morris, Ronald Sydney Nyholm, Colin Sydney Ralph, Aubrey James Tow, Douglas Elwood White, Alan Maynard Willison, Robert Thompson Wade.

The following donations were received : 318 parts of periodicals, and 29 whole volumes.

Notice of Motion.—Dr. F. Lions moved that the Council be asked to proceed with the selection of a Liversidge Lecturer for the year 1940.

A lecturette illustrated by lantern slides, and entitled " Highlights of a Recent World Tour ", was given by Mr. A. R. Penfold.

The following papers were read :

" The Preparation and Properties of Some Diazoaminoazo Compounds ", by F. P. Dwyer, M.Sc.

" Coordination Compounds with Furfuraldoxime as a Chelate Group. Part I. Additional Compounds with Metallic Salts ", by A. Bryson, M.Sc., B.App.Sc., and F. P. Dwyer, M.Sc.

" A New Synthesis of Nor-Nicotyrine, and of its Oxygen Analogue", by Francis Lions, B.Sc., Ph.D., and Ernest Ritchie, M.Sc.

" The Constitution of Gmelinol. Part II ", by Rita H. Harradence, M.Sc., and Francis Lions, B.Sc., Ph.D.

" Magnetic Studies of Coordination Compounds. Part II. The Effect of Distortion of Valence Bond Angles in Nickel and Palladium Derivatives of Substituted Pyrromethenes ", by D. P. Mellor, M.Sc., and W. H. Lockwood, B.Sc.

" The Significance of Large Bond Angle Distortions in Relation to the Stereochemistry and Magnetic Properties of Quadricovalent Metals ", by D. P. Mellor, M.Sc.

" The Segre Quartic Surface with Four Nodes ", by Professor T. G. Room, M.A.

July 3, 1940.

The five hundred and seventy-ninth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Professor A. P. Elkin, President, was in the chair. Thirty-eight members and one visitor were present. The minutes of the preceding meeting were read and confirmed.

The certificates of seven candidates for admission as ordinary members of the Society were read for the first time.

The certificates of twenty-eight candidates for admission as ordinary members of the Society were read for the second time.

The following persons were duly elected ordinary members of the Society : Victor John Callanan, Maxwell Clark Chambers, Samuel Bernard Cohen, Beverly Cortis-Jones, Morris Edward Cox, Anthony Dadour, Franklin Charles Finch, Thomas Harley Johns, William Walter Kennard, Leonard Esmond King, Gordon James Lincoln, Albert Anthony Luciano, Margaret Elphinstone Maccoll, William Stewart Ainsworth McGowan, Brian James McGrath, Gordon Howard McGregor, Edward E. Malone, William Millership, Alban James Moore Murray, William Walter Pettingell, Rutherford Ness Robertson, Sidney Rosenbaum, Jean Elizabeth Ross, Reginald Henry Scott, Eric Brian Jeffcoat Smith, Richard Harris Stroud, James Vernon, Samuel James Wogan.

The following donations were received : 126 parts of periodicals, and 9 whole volumes.

Motion from May Meeting.—Professor A. P. Elkin, the President, moved that the following alterations to Rule VIII be approved :

"That the following paragraphs be substituted for paragraph 4, Rule VIII :

"'The certificate shall be delivered to the Honorary Secretary and shall be considered at the Council Meeting next ensuing after its receipt. The names of the candidate and proposers shall be circulated to all members before each of the two following Ordinary General Meetings of the Society. The certificate shall be read at those meetings and during the interval between them shall be exhibited in a conspicuous place in one of the rooms of the Society.

"' It shall be competent for a nominator to withdraw his support of a candidate at any time up to the second reading of the certificate by notice given in writing to the Honorary Secretary of the Society. Such withdrawal shall render the certificate informal.' "

The motion was seconded by Mr. Le Souef, and carried unanimously.

The following papers were read :

"Experiments on the Synthesis of the Pyridine Analogue of Vitamin B (Aneurin) ", by Rita H. Harradence, M.Sc., and Francis Lions, B.Sc., Ph.D.

"The Isomerism of Diazoaminoazo Compounds ", by F. P. Dwyer, M.Sc.

"The Corals of the Garra Beds, Molong District, N.S.W.", by Dorothy Hill, M.Sc., Ph.D., and O. A. Jones, M.Sc.

A lecturette, illustrated with lantern slides, and entitled " Submarine Canyons ", was given by Dr. G. D. Osborne.

August 7, 1940.

The five hundred and eightieth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Professor A. P. Elkin, President, was in the chair. One hundred and six members and visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificates of seven candidates for admission as ordinary members of the Society were read for the second time.

The following persons were duly elected as ordinary members of the Society : Alan Charles Brigden, Lindsay Arthur Buckley, Edward Ritchie Cole, Joyce Marie Cooper, Robert Fisher, Daphne M. Little, Jack Campbell Norrie.

The following donations were received : 248 parts of periodicals, 11 back numbers, and 26 whole volumes.

Motion from last Meeting.—It was moved by the President that the following alteration should be approved :

"That the following paragraphs be substituted for paragraph 4, Rule VIII :

"' The certificate shall be delivered to the Honorary Secretary and shall be considered at the Council Meeting next ensuing after its receipt. The names of the candidate and proposers shall be circulated to all members before each of the two following Ordinary General Meetings of the Society. The certificate shall be read at those meetings and during the interval between them shall be exhibited in a conspicuous place in one of the rooms of the Society.

" ' It shall be competent for a nominator to withdraw his support of a candidate at any time up to the second reading of the certificate by notice given in writing to the Honorary Secretary of the Society. Such withdrawal shall render the certificate informal.' "

This was seconded by Mr. Ollé and carried unanimously.

The following papers were read :

"Furfuraldoxime as a Chelate Group. Part II. Palladium Compounds with α (syn.) Furfuraldoxime ", by A. Bryson, B.Sc.App., M.Sc., and F. P. Dwyer, M.Sc.

"The Lower Middle Devonian Rugose Corals of the Murrumbidgee and Goodradigbee Rivers, N.S.W.", by Dorothy Hill, M.Sc., Ph.D.

"Elementary Presentation of the Frequency Distributions of Certain Statistical Populations Associated with the Normal Population ", by D. T. Sawkins, M.A., B.A. (Cambridge). (Communicated by Professor T. G. Room.)

These papers were read by title only :

Symposium.

A symposium on " Potassium " was held, the speakers being as follows :

1. " The Commercial Potash Situation in Australia ", G. de Vahl Davis, B.Sc.Agr.
2. " Some Aspects of the Chemistry of Potassium, with Special Reference to Potential Sources in Australia ", D. P. Mellor, M.Sc.
3. " Potassium in Soil ", N. H. Parbery, D.Sc.
4. " Potassium in Plants ", R. N. Robertson, B.Sc., Ph.D., *vice* Professor E. Ashby, D Sc.

A film entitled " The Mining and Manufacture of Potash in Europe " was shown by Mr. G. de Vahl Davis.

A discussion followed the addresses, those taking part being Professor L. A. Cotton, Professor R. D. Watt, Mr. R. S. Morris, Mr. M. R. Freney, Dr. R. K. Murphy, Mr. J. W. Hogarth and Mr. G. de Vahl Davis.

September 4, 1940.

The five hundred and eighty-first General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Professor A. P. Elkin, President, was in the chair. Thirty-two members and one visitor were present. The minutes of the preceding meeting were read and confirmed. The President announced the deaths of the following members : Henry Herbert Baker, a member since 1919, and John Patrick O'Neill, a member since 1932.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Margaret Joyce Colditz, and Henry James Emmerton.

The following donations were received : 149 parts of periodicals, and 16 whole volumes.

The following papers were read :

" Radial Heat Flow in Circular Cylinders with a General Boundary Condition ", by J. C. Jaeger, B.Sc., M.A. (Communicated by Professor H. S. Carslaw.)

" The Essential Oils of *Eucalyptus australiana* (Baker and Smith) and its Physiological Forms ", Part III, by A. R. Penfold, F.A.C.I., F.C.S., and F. R. Morrison, A.A.C.I., F.C.S.

" Arenaceous Foraminifera from the Permian Rocks of N.S.W.", by Irene Crespin, B.A., and W. J. Parr, F.R.M.S. (Communicated by Dr. Ida A. Brown.)

" The Stratigraphy and Structure of Silurian and Devonian Rocks of the Yass-Bowning Districts, N.S.W.", by Ida A. Brown, D.Sc.

Paper for Discussion.—The following paper, read by title at the last meeting, was open for discussion :

" Elementary Presentation of the Frequency Distributions of Certain Statistical Populations Associated with the Normal Population ", by D. T. Sawkins, M.A., B.A. (Cambridge). (Communicated by Professor T. G. Room.)

Exhibits.—Exhibits shown by Professor A. P. Elkin were two sacred stones and two bull-roarers.

Exhibits shown by Mr. A. R. Penfold were of glass textiles.

October 2, 1940.

The five hundred and eighty-second General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Professor A. P. Elkin, President, was in the chair. Forty-six members and two visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The President announced that the Third Liversidge Research Lecture to be given under the auspices of the Royal Society of New South Wales would be delivered on Thursday, October 31st, 1940, at Science House, Sydney, by Mr. G. J. Burrows, B.Sc., and would be entitled " Organic Arsenicals in Peace and War ".

The following donations were received : 111 parts of periodicals, 28 back numbers, and 5 whole volumes.

The following papers were read :

" The Detection and Estimation of α-Terpinene by Means of the Diene Synthesis ", by R. M. Gascoigne, B.Sc.

" The Fission of the Cyclopropane Ring of α-Thujene ", by R. M. Gascoigne, B.Sc.

" A Direct Synthesis of 1 : 2 : 4 : 5-Tetra-substituted Iminazoles ", by Francis Lions, B.Sc., Ph.D., and Ernest Ritchie, M.Sc.

A lecturette entitled " The Early History of Wireless ", illustrated by lantern slides, was given by Mr. G. G. Blake, M.I.E.E., F.Inst.P.

November 6, 1940.

The five hundred and eighty-third General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Dr. H. S. Halcro Wardlaw, Vice-President, was in the chair. Sixty-one members and three visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members were read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Joan Marian Crockford, Robert James Anning Franki, John Nevil Graves, and Carlyle Joseph Sarroff.

The following donations were received : 165 parts of periodicals, and 5 whole volumes.

Notices of Motion.—Dr. H. S. Halcro Wardlaw gave notice of motion for the next general meeting, with regard to proposed alterations to the Rules, to provide for a postal ballot.

Dr. F. Lions also gave notice of motions concerning the alteration of the Rules.

The following papers were read :

"The Action of Hydrogen and Raney-nickel on Some Aromatic Aldehydes ", by Adrien Albert, Ph.D., B.Sc., and B. Ritchie, B.Sc.

"Australian Triassic Fishes ", by R. T. Wade, M.A., Ph.D.

"Permian Bryozoa of Eastern Australia ", Part I, " A Description of Some Previously-named Species of Fenestrellidinæ (Fenestrellidæ) ", by Joan Crockford, B.Sc. (Communicated by Dr. Ida Brown.)

"A Note on Some Leucite-bearing Rocks from N.S.W., with Special Reference to an Ultrabasic Occurrence at Murrumburrah ", by Madeleine H. Harvey, B.Sc., and Germaine A. Joplin, B.Sc., Ph.D.

December 4, 1940.

The five hundred and eighty-fourth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Professor A. P. Elkin, President, was in the chair. Sixty-five members were present. The minutes of the preceding meeting were read and confirmed.

Certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Ronald Stuart Clarke and Gordon Collett.

Business Arising Out of Minutes.—The Honorary Secretary reported that the sub-committee appointed to consider the proposals for a postal ballot had approved in principle that the Rules should be amended to provide for a postal ballot for election of officers of Council, but that the question of machinery for giving effect to the proposal was deferred, as no agreement could be reached.

The following donations were received : 222 parts of periodicals, and 10 whole volumes.

The following papers were read :

"The Thermal Decomposition of Ethylidene Bromide ", by P. T. Bennett and A. Maccoll, M.Sc.

"A Note on the Transformation of β Furfuraldoxime to Furamide", by A. Bryson, M.Sc., B.App.Sc., and F. P. Dwyer, M.Sc.

"Coordination Compounds with Furfuraldoxime as a Chelate Group ", Part III, " Complex Metallic Derivatives of β (anti) Furfuraldoxime ", by A. Bryson, M.Sc., B.App.Sc., and F. P. Dwyer, M.Sc.

"Magnetic Studies of Coordination Compounds", Part III
   "Factors Affecting the Nature of Bonds Between Nickel and
   Certain Non-Metallic Atoms", by D. P. Mellor, M.Sc., and
   D. P. Craig.   Part IV, "Square Coordinated Cobaltous
   Compounds", by D. P. Mellor, M.Sc., and D. P. Craig.

"1-Hydroxyacridine as a Chelate Compound", by D. H. Freeman,
   B.Sc., and F. Lions, B.Sc., Ph.D.

"Synthetic Experiments with 3- and 4-Aminoquinaldines", by
   F. Lions, B.Sc., Ph.D., and E. Ritchie, M.Sc.

"Isolation of a Toxic Principle from the Seeds of Macrozamia
   spiralis", by Joyce M. Cooper, M.Sc.

"Permian Bryozoa of Eastern Australia", Part II, "New Species
   from the Upper Marine Series of New South Wales", by
   Joan M. Crockford, B.Sc.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

GEOLOGY

Chairman : Dr. H. G. Raggatt.*

Honorary Secretary : R. O. Chalmers.

Eight meetings were held during the year, the average attendance being twelve members and four visitors.

April 19th.—Exhibits : By Dr. G. D. Osborne : (*a*) Contact limestone from Crestmore, California, containing merwinite, spurrite, monticellite, crestmoroite, vesuvianite, wollastonite and dumortierite ; (*b*) Brucite after periclase from a small pegmatite dyke. By Mr. R. O. Chalmers : (*a*) Photographs of folded and faulted ore-bearing slate from Mount Isa, Queensland ; (*b*) Banded rock showing folding and faulting, from Lochinvar, N. S. Wales. By Miss Quodling : Using a light source, the convergent system from a microscope, and two polaroid films, excellent interference figure were projected of a size quite visible to the naked eye. By Dr. Anderson : Fossil fish, *Cleithrolepis granulata*, from the Triassic (Hawkesbury shale) at Woronora Dam. Similar fish have been found at Brookvale, Gosford, and St. Peters. By Mr. H. O. Fletcher : (*a*) A crinoid from the Varney Parkes collection found at Ulladulla, N.S.W. The species is *Tribrachiocrinus clarkei*, and the pinnules are preserved, a rare occurrence ; (*b*) A large species of *Limulus* from Beacon Hill quarry, Brookvale. It differs from the few already described in that the genal spines of the cephalothorax project outward instead of following the body contour. By Dr. Ida Brown : (*a*) *Terebratula* from America showing colour markings ; (*b*) Starfish, *Australaster stutchburia*, from Jervis Bay. By Dr. Joplin : On behalf of Mr. Gibson, a concretion from Mudgee resembling somewhat a septarian nodule. By Mr. Lambeth : Mention of a spring depositing iron oxide in Por. 7, Ph. Belanglo, Mittagong. This problem was discussed by Drs. Raggatt and Anderson, and Mr. Andrews, the latter speaker favouring the long distance origin of springs. By Dr. H. G. Raggatt : (*a*) A sheared piece of porphyry, shaped like an aboriginal axe, from Bobadah, 300 miles due west of Sydney. (*b*) Quartz chips cemented in ironstone by iron oxide, from a fossil terrace round Lake George on the Southern Highlands.

May 10th.—Address by Dr. G. D. Osborne, " Some Modern Trends in Geological Research Abroad ".

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* Very shortly after the annual meeting Dr. Raggatt took up a position in Canberra, and for the greater part of the year Dr. A. B. Walkom was Acting Chairman.

June 28th.—Address by Mr. L. Owen, " Freak Oil Fields ".

August 2nd.—Exhibits : By Mr. J. A. Dulhunty : Sand from the Central Australian deserts. The colour of all sand, dust, and soil in this area is red. By Dr. Ida Brown : The blastoid found by Dr. Case in the Branxton railway cutting, and since lost for many years. It is most probably an internal cast of *Calicocrinus*, described also from Timor. By Mr. H. O. Fletcher : (*a*) *Keenia twelvetreesi* from the Permian of Tasmania. The characters of the body whorl are not typical of *Keenia*. The type specimen of *Keenia* from Allandale is a larger shell and has a more straight-sided body whorl ; (*b*) *Nuculana* from the Lower Bowen series, characterised by zigzag sculpturing. Recent specimens of *Nuculana* have not this feature, and it is thought that the Lower Bowen specimen is a new genus. By Mr. T. Hodge-Smith : The Tawallah Valley siderite, a nickel-rich ataxite from the Northern Territory.

August 30th.—Address by Mr. R. O. Chalmers, " The Building Stones of Sydney ".

September 27th.—Address by L. Owen, " Notes on the Phosphate Deposit of Ocean Island, with Remarks on the Phosphates of the Equatorial Belt of the Pacific Ocean ".

November 1st.—Address by Mr. J. M. Rayner, " Geophysics as Applied to Geological and Mining Problems ".

November 29th.—Address by Dr. G. D. Osborne, " The Bullahdelah Alunite Deposits ".

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

INDUSTRY

Chairman : A. D. Ollé, F.C.S., A.A.C.I.

Visits were made during the year to the following :
1940.

June 12.—Carpet Manufacturers Limited, 12-27 Harris Road, Five Dock.

July 9.—Amalgamated Wireless of Australasia, York Street, Sydney, new building.

September 10.—Division of Wood Technology, of the Forestry Commission of New South Wales, 96 Harrington Street, Sydney.

October 8.—Hygienic Containers, Gardener's Road, Alexandria.

November 12.—Eveready Australia Pty. Limited, Harcourt Parade, Rosebery.

INDEX.

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